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ONTARIO RESEARCH FOUNDATION

CANMET

SYMPOSIUM

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MINERAL FILLERS

Applications, Specifications, Traditional and Substitute Materials

in conjunction with the
Canadian Mining and Aggregate
Equipment Exhibition

Toronto

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ONTARIO**RESEARCH**
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CANMET

SYMPOSIUM

INTRODUCTION

E.C. BROWN

ONTARIO RESEARCH FOUNDATION
MISSISSAUGA, ONTARIO

INTRODUCTION

E.C. BROWN

ONTARIO RESEARCH FOUNDATION

It was the pleasure of Ontario Research to organize a two-day symposium on Mineral Fillers for CANMET of Energy, Mines and Resources in Ottawa. We are grateful to the Southex Organization which coordinated the equipment show and was cooperative and helpful in assisting with the organization of the seminar. Specifically, our thanks are due to Ron Collings of CANMET and Jacob Leidner of Ontario Research who organized the seminar.

We glibly speak often of the need for interdisciplinary approaches to problem solving and of the need to bridge the R & D/Industry interface. In this area of mineral fillers, it appears that the resolution of these problems is critical to continued technical developments and application of new developments to industry. The problem is enhanced by the involvement of two general types of industry (as in many other areas), the producers and the users. The producers are diverse, including those who produce materials suitable for fillers in a deliberate manner and those who produce them accidentally. The accidental or non-deliberate production has in some cases posed environmental problems and, thereby, contributed to the rapidly developing waste materials industry. In addition, the users represent a wide variety of materials and products with diverse requirements - cost reduction, improved mechanical properties, enhanced appearance, etc.

If we superimpose on that picture the perspectives of R & D, there are studies of particle size and shape, knowledge of effects on physical properties, questions of interfacial properties (organic/inorganic incompatibilities), questions of interfacial reactions (e.g. pozzolanic or hydraulic cement reactions), problems of energy conservation in production, engineering requirements of handling and processing fine particles, and, in general, the requirement to match materials to use or the need to modify materials to meet existing requirements.

The need for an interdisciplinary, cooperative approach to the business opportunities inherent in this mix of factors is obvious.

The seminar program included an excellent group of speakers and a selection of papers which touched on and amplified the factors that have been briefly mentioned. Further, the audience included those whose interests and knowledge contributed considerably to the discussions. It is felt, therefore, that the following papers succeeded in producing interesting new perspectives for the study and utilization of this class of interesting materials we call "Mineral Fillers".

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ONTARIO RESEARCH FOUNDATION

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SYMPOSIUM

REMARKS ON ONTARIO'S MINERAL FILLERS

G. GEOFFRY MINNES

INDUSTRIAL MINERALS SECTION
MINISTRY OF NATURAL RESOURCES
TORONTO, ONTARIO

REMARKS ON ONTARIO'S MINERAL FILLERS

JOINT SYMPOSIUM ON
MINERAL FILLERS

SPONSORED BY:
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THE CANADIAN MINING AND AGGREGATE
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TORONTO, ONTARIO
OCTOBER 20 & 21, 1981

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INDUSTRIAL MINERALS SECTION
MINISTRY OF NATURAL RESOURCES

REMARKS ON ONTARIO'S MINERAL FILLERS

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INDUSTRIAL MINERALS SECTION
MINISTRY OF NATURAL RESOURCES

INTRODUCTION

A MEETING OF THIS SORT IS MOST TIMELY AND A 'FIRST' OF ITS KIND THAT I HOPE WILL BE REPEATED FREQUENTLY IN THE FUTURE. IT IS A PLEASURE TO SEE THAT WHILE THE GENERAL CONTENT OF THIS SYMPOSIUM IS DIRECTED TOWARD MINERALS, WE WILL ALSO HAVE AN OPPORTUNITY TO LEARN OF RECENT ACTIVITIES BY THOSE SEEKING USES FOR MATERIALS SO INTRIGUING AS ASBESTOS TAILINGS, FLY ASH AND CEMENT KILN DUST.

THIS MEETING COVERS A BROAD SPECTRUM RANGING FROM MATERIALS CONSIDERED AS WASTES, PRIMARILY FROM THE MINING SECTOR, ON WHICH MR. R.K. COLLINGS AND CANMET HAVE DONE SO MUCH WORK AND DIRECTED ATTENTION DURING THE PAST SEVEN OR MORE YEARS TO THE VERY USEFUL ACTIVITY OF DR. R.G.W. LAUGHLIN OF THE ONTARIO RESEARCH FOUNDATION WHOSE WASTE EXCHANGE PROGRAM HAS SUCCESSFULLY HIGHLIGHTED THE AVAILABILITY OF NUMEROUS WASTES FROM MANUFACTURING COMPANIES ACROSS THE COUNTRY. BOTH ORGANIZATIONS HAVE VERY LONG AND HONOURED HISTORIES IN THE DEVELOPMENT OF INDUSTRIAL MINERAL MINES AND PRODUCTS IN CANADA.

WITHIN THE TIME AVAILABLE THIS MORNING I WISH TO ACQUAINT YOU WITH SOME OF THE MANY INDUSTRIAL MINERALS OF ONTARIO THAT ARE SUITABLE FOR MINERAL FILLERS AND EXTENDERS.

THE SCENE

THE SPECTRUM OF MINERAL FILLERS IS BROAD AND EMBRACES MANY NATURAL AND SYNTHETIC COMPOUNDS. THE PRINCIPLE OBJECTIVES IN

USING THEM ARE TO REDUCE THE OVERALL COST OF FINISHED PRODUCTS AND TO INTRODUCE SOME PROPERTIES THAT ENHANCE THE USEFULNESS OF THOSE PRODUCTS. WE HAVE MANY OF THE REQUIRED MINERALS HERE IN ONTARIO AND SOME ARE MORE SUITED TO DEVELOPMENT THAN OTHERS. WE HAVE BARITE, CALCITE, KAOLIN, MICA, NEPHELINE SYENITE, SILICA, TALC, TO NAME SOME OF THE MORE OBVIOUS. IT MIGHT BE EASIER TO DESCRIBE THE SITUATION BY SAYING THAT FEW OF THE MAJOR MINERAL FILLERS AND EXTENDERS ARE NOT FOUND SOMEWHERE IN ONTARIO.

OF THE ESTIMATED $289,4 BILLION GROSS CANADIAN NATIONAL PRODUCT IN 1980 OVER 41 PERCENT WAS GENERATED IN ONTARIO WHILE WITHIN 160 Km OF TORONTO RESIDES ABOUT ONE THIRD OF THE NATION'S BUYING POWER. SUCH CONCENTRATION OF THE ECONOMY POSES BOTH CHALLENGES AND OPPORTUNITIES FOR MINERAL PRODUCERS.

THE SINGLE FACTOR OF GREATEST SIGNIFICANCE TO PRODUCERS AND CONSUMERS OF MINERAL FILLERS THAT HAS EMERGED IN THE PAST 8 YEARS OR SO IS THE COST OF ENERGY AND ITS IMPACT ON ALL OF NORTH AMERICA. THE RAPID ESCALATION IN PETROLEUM PRICES HAS MEANT MUCH HIGHER TRANSPORTATION COSTS AND HIGHER ENERGY COSTS TO PROCESS MINERAL FILLERS.

ONTARIO MINERAL PRODUCTION

THE VALUE OF MINERAL PRODUCTION IN ONTARIO IN 1980 WAS ESTIMATED AT $4.68 BILLION OF WHICH SOME $776 MILLION WAS REPRESENTED BY NONMETALLIC MINERALS AND STRUCTURAL MATERIALS. OF THIS LATTER

TABLE: Ontario mineral production, Selected Years, 1950, 1979 & 1980

		1950(1)		1979(1)		1980(2)	
	UNIT	QUANTITY	VALUE $	QUANTITY	VALUE $	QUANTITY	VALUE $
Non-metals							
Arsenic	tonne	-	16,220	-	-	-	-
Asbestos	tonne	9,590	1,493,039	-	-	-	-
Barite	tonne	-	-	-	596,000	-	750,000
Feldspar	tonne	5,224	49,619	-	-	-	-
Fluorspar	tonne	7,816	262,643	-	-	-	-
Gemstones	kg	-	-	-	65,454	-	70,000
Graphite	tonne	-	390,815	-	-	-	-
Gypsum	tonne	180,778	875,217	743,511	4,831,117	793,000	7,488,000
Mica-amber	kg	441,336	28,299	-	-	-	-
-muscovite	kg	85,630	128,161	-	-	-	-
Nepheline syenite	tonne	-	842,886	605,699	15,180,042	592,000	15,877,000
Peat	tonne	5,091	206,625	7,035	675,547	8,000	815,000
Phosphate	tonne	-	712	-	-	-	-
Quartz	tonne	1,257,858	1,027,791	980,279	8,965,420	1,294,000	10,108,000
Salt	tonne	631,780	4,639,867	5,188,664	67,900,216	4,800,000	72,358,000
Soapstone, talc, pyrophyllite	tonne	13,844	182,048	-	914,257	-	1,025,000
Sulphur in smelter gas	tonne	-	131,540	315,992	6,221,013	525,000	13,542,000
Sulphur, elemental	tonne	-	-	20,293	673,199	22,000	1,200,000
Total, non-metals			10,275,482		106,022,265		123,233,000
Structural materials							
Clay products	tonne	-	9,323,263	-	60,767,493	-	59,527,000
Cement	tonne	843,389	10,953,896	4,117,179	182,252,209	4,283,000	225,594,000
Lime	tonne	518,341	6,030,228	1,317,944	51,920,880	1,295,000	60,590,000
Sand and gravel	tonne	27,462,358	15,553,186	90,515,630	151,847,457	121,254,000(3)	174,900,000
Stone	tonne	5,184,465	7,843,124	39,830,992	113,477,990	34,019,000(3)	132,000,000
Total, structural materials			49,703,697		560,266,029		652,611,000
Total, industrial minerals			59,979,179		666,288,294		775,844,000
Total, metals			302,540,548		2,544,643,588		3,869,293,000
Total, fuels			9,783,447		29,679,000		34,935,000
Grand total for Ontario			372,303,174		3,240,610,882		4,680,072,000

Source: (1) Mineral Statistics, Ministry of Natural Resources
(2) MNR/EMR - Estimate
(3) Projection Only: Not based on Industry estimates.

FIGURE APPROXIMATELY 84 PERCENT WAS STRUCTURAL MATERIALS, NEARLY 9.3 PERCENT WAS SALT AND THE REMAINDER OTHER NONMETALLIC MINERALS. TABLE 1 SHOWS MINERAL PRODUCTION BY CATEGORY, ESTIMATES FOR 1980, ACTUAL FIGURES FOR 1979 AND ALSO FOR 1950 JUST TO SHOW THE MAGNITUDE OF GROWTH IN PRODUCTION AND VALUE. THERE HAS BEEN A 12 FOLD INCREASE IN VALUE OF NON-METALS PRODUCTION AND A 13 FOLD INCREASE IN THE VALUE OF STRUCTURAL MATERIALS PRODUCTION OVER THE PAST 30 YEARS.

NO SPECIFIC BREAK-DOWN OF PRODUCTION OR CONSUMPTION OF MINERAL FILLERS IS AVAILABLE AS FAR AS I KNOW. THE AMOUNTS MUST BE RELATIVELY SMALL EVEN IF WE WERE TO INCLUDE THE STONE DUST INCORPORATED INTO VARIOUS TYPES OF ROADS. HOWEVER WE ARE NOT SO MUCH CONCERNED ABOUT THE PRESENT AMOUNTS AS THE WIDE RANGE OF MATERIALS AVAILABLE, THE RESEARCH OVER MANY YEARS DEVOTED TO DEVELOPING NEW USES FOR ONTARIO MINERALS, THE PERSISTENT DRIVE OF THE DEVELOPERS OF ONTARIO INDUSTRIAL MINERAL RESOURCES AND THE OPPORTUNITIES FACING US FOR NEW DEVELOPMENT TO MEET CHANGING ECONOMIC CIRCUMSTANCES.

MARKET AREA

ONTARIO IS PART OF AN ENORMOUS MARKET TERRITORY, THE SIZE OF WHICH IS SOMETIMES NOT FULLY RECOGNIZED BECAUSE OF POLITICAL BOUNDARIES THAT EXIST. ONTARIO'S OWN POPULATION IS 8.5 MILLION AND I HAVE ALREADY NOTED THE PROVINCE GENERATED IN 1980 ABOUT 41 PERCENT OF

THE ENTIRE CANADIAN GROSS NATIONAL PRODUCT ESTIMATED TO BE $289,4 BILLION. WITHIN 160 KILOMETRES OF TORONTO LIES ABOUT ONE THIRD OF THE NATION'S BUYING POWER. TO THIS ONE CAN ADD QUEBEC'S 6.3 MILLION PEOPLE AND THE NEARLY 30 PERCENT OF THE CANADIAN G.N.P. ORIGINATING THERE. IF WE FURTHER ADD THE NEARLY 100 MILLION PERSONS IN THE NEARBY 15 STATES BETWEEN MAINE AND MINNESOTA AND THE 55 PERCENT OF THE TOTAL AMERICAN VALUE ADDED BY MANUFACTURE THAT WAS GENERATED IN THOSE STATES WE CERTAINLY HAVE A SIZEABLE MARKET. I WOULD HAVE TO THINK THAT ANY PRODUCER OF MINERAL FILLERS IS FACED WITH CERTAIN ADVANTAGES AND DISADVANTAGES WITH RESPECT TO THE MARKET AREAS AND THAT WITH ONE OR TWO EXCEPTIONS ONTARIO DEPOSITS AND PRODUCERS ARE WELL SITUATED TO MEET MARKET CONDITIONS THAT WILL FACE US IN THE FUTURE. IT MAY WELL BE THAT THE OPTIMUM SIZE OF OPERATION WILL BE SMALLER THAN WE MIGHT LIKE OR THE PORTION OF THE MARKET SERVED MAY BE SOMEWHAT RESTRICTED BUT THAT SHOULD NOT KEEP US FROM TAKING ADVANTAGE OF EVERY OPPORTUNITY AFFORDED US.

USES

THE MAJOR MEDIUM TO HIGH VALUE END-USES FOR MINERAL FILLERS AND EXTENDERS, AS YOU KNOW, ARE PRINCIPALLY IN THE THE FOLLOWING AREAS-PAINT, PAPER, PLASTICS, PUTTY,CAULKS AND SEALANTS, RUBBER, ADHESIVES AND CARPET BACKING, PLUS A WHOLE HOST OF LESSER APPLICATIONS THAT IN TOTAL REPRESENT SIZEABLE MARKETS FOR MINERAL PRODUCERS. AN EXCELLENT STUDY OF MINERAL FILLERS AND EXTENDERS

COMPLETED BY C.H. KLINE CO.,INC. IN 1978 FORECAST U.S. CONSUMPTION BY 1982 OF MINERIAL FILLERS AND EXTENDERS AMOUNTING TO 7,75 MILLION TONS VALUED IN 1977 DOLLARS AT $670 MILLION WHILE 1977 CONSUMPTION WAS ESTIMATED AT 6.1 MILLION TONS VALUED AT $520 MILLION. KAOLIN REPRESENTED 50 PERCENT AND CALCIUM CARBONATE 30 PERCENT OF THE TOTAL TONNAGE PRODUCED WHILE THEY REPRESENTED 36 PERCENT AND 14.6 PERCENT RESPECTIVELY OF THE TOTAL VALUE.

MINERAL FILLER PRODUCERS

I HOPE EVERYONE AGREES THAT WHEN WE TALK OF FILLERS WE ALSO INCLUDE EXTENDERS BECAUSE NONE OF THE MATERIALS I PLAN TO MENTION ARE STRICTLY FILLERS. FEW IF ANY ONTARIO DEPOSITS HAVE BEEN CONSIDERED OR DEVELOPED SOLELY FOR THEIR EXTENDER/FILLER POTENTIAL. MOST THAT I AM AWARE OF HAVE BEEN OR WOULD BE DEVELOPED WITH OTHER MARKETS OF PRIMARY IMPORTANCE WHILE FILLER APPLICATIONS ARE ADDITIONAL TO THE ORIGINAL DEVELOPMENTAL PURPOSES.

NEPHELINE SYENITE

ONE WOULD HAVE TO RATE NEPHELINE SYENITE AS THE MOST IMPORTANT ONTARIO MINERAL FILLER IN TERMS OF TONNAGE AND VALUE. INDUSMIN LIMITED HAS BEEN THE LEADER WORLD-WIDE IN DEVELOPING NEW FILLER AND EXTENDER USES FOR NEPHELINE SYENITE THROUGH THE YEARS FROM A START IN THE EARLY 1950's. I RECALL THAT THE ONTARIO RESEARCH FOUNDATION PREPARED A REPORT ENTITLED "NEPHELINE SYENITE AS AN EXTENDER PIGMENT FOR PAINT" - BY W.N.B. ARMSTRONG AND V.K. CROUTEN IN 1957,THE RESULTS OF MORE THAN 6 YEARS EXPOSURE OF NEPHELINE

SYENITE BASED PAINTS. INDUSMIN HAS EXAMINED NEW POTENTIAL USES FOR MICRON-SIZED NEPHELINE SYENITE AND NOW HAS A PRODUCT RANGE COVERING MINEX 2, 3, 4, 7 AND 10 WITH TOP SIZES FROM 74 MICRON DOWN TO FINER THAN 10 MICRON. RECENTLY, INTERNATIONAL MINERALS AND CHEMICAL CORPORATION COMPLETED INSTALLATION OF FACILITIES TO PRODUCE APEX 400 AND APEX 700 FILLER GRADES OF PRODUCTS AND WE WILL HOPE THIS PRESAGES A BURST OF GROWTH FOR BOTH COMPANIES IN THIS INTERESTING FIELD.

NEPHELINE SYENITE BRINGS MANY EXCELLENT PROPERTIES TO COATINGS AND PLASTICS MORE IMPORTANTLY, ITS INERTNESS TO WEATHERING, AN INDEX OF REFRACTION SO SATISFACTORY IN POLYVINYL CHLORIDE APPLICATIONS, ITS WHITENESS AND UNIFORM HIGH DRY BRIGHTNESS, LOW VEHICLE DEMAND, PH STABILITY, LACK OF FREE SILICA, AND GOOD DISPERSION.

OVER THE YEARS OTHER NEPHELINE SYENITE DEPOSITS HAVE BEEN EVALUATED PARTICULARLY IN THE BANCROFT AND PORT COLDWELL AREAS OF THE PROVINCE. CURRENTLY ONE COMPANY IS STUDYING THE LARGE DEPOSITS IN BIGWOOD TOWNSHIP FOR POSSIBLE DEVELOPMENT IN WHICH CASE PERHAPS OPPORTUNITIES FOR NEW FILLER APPLICATIONS COULD EMERGE.

CALCITE WHITING

WHEN THE W.R. BARNES LIMITED PLANT AT PERTH BEGAN OPERATIONS IN 1978 ONTARIO HAD ITS FIRST LARGE-SCALE PRODUCER OF ULTRA-WHITE MICRON-SIZED CALCITE WHITING. THE PLANT HAS A CAPACITY OF SOME 200,000 TONNES OF CLOSELY SIZED CALCITE PRODUCTS RANGING FROM

COARSE AGGREGATES TO FINE SANDS TO LOW MICRON SIZED POWDERS THAT SERVE MANY DIFFERENT MARKETS. COMING ONSTREAM AT ABOUT THE SAME TIME MAJOR CHANGES WERE TAKING PLACE IN THE OWNERSHIP AND CAPACITIES OF AMERICAN PRODUCERS OF SIMILAR PRODUCTS REQUIRED A MEASURE OF CONFIDENCE BY THE BARNES ORGANIZATION THAT IS BEING JUSTIFIED IN THE MARKET PLACE. SUFFICIENT CONFIDENCE WAS IN FACT SHOWN THAT THE VENTURE WAS ACQUIRED IN EARLY 1981 BY STEEP ROCK IRON MINES LTD., PART OF THE C.P. ENTERPRISES LIMITED GROUP OF COMPANIES.

ORE RESERVES ARE LARGE AT THE TATLOCK PROPERTY WHERE CALCITE IS MINED AND THE COMPANY IS WELL SITUATED TO SERVE A VERY WIDE MARKET AREA AND RANGE OF INDUSTRIES. THE FACILITIES AT THE MINE AND PLANT ARE HIGHLY FLEXIBLE TO MEET CHANGING MARKET NEEDS AND ONE CAN EXPECT THIS COMPANY TO BE A MAJOR SUPPLIER OF WHITE CALCIUM CARBONATE IN THE YEARS AHEAD.

TALC

ONTARIO HAS TWO PRODUCERS OF TALC EACH PROVIDING DISTINCTLY DIFFERENT PRODUCTS THAT SERVE A WIDE RANGE OF MARKETS AND INDUSTRIES. CANADA TALC INDUSTRIES LIMITED, WHICH WAS RECENTLY ACQUIRED BY W.R. BARNES LIMITED, OPERATES AN UNDERGROUND MINE NEAR MADOC THAT HAS BEEN IN CONTINUOUS PRODUCTION SINCE 1896. THE TALC ORE WHICH ALSO CONTAINS SOME DOLOMITE AND MINOR AMOUNTS OF OTHER SILICATES IS CRUSHED, DRY-GROUND, AIR CLASSIFIED, BAGGED AND SOLD FOR USE IN PAINT, TILE, LINOLEUM, RUBBER AND OTHER FILLER APPLICATIONS. TOTAL CURRENT ANNUAL PLANT CAPACITY FOR TALC

PRODUCTION IS ABOUT 18,000 TONNES BUT CANADA TALC IS ALREADY PLANNING TO PRODUCE NEW PRODUCTS TO MEET A WIDER RANGE OF MARKET NEEDS. THE COMPANY ALSO PRODUCES FINE GROUND DOLOMITE WHITING FOR CERTAIN FILLER APPLICATIONS.

STEETLEY TALC LIMITED, A SUBSIDIARY OF STEETLEY INDUSTRIES LIMITED OF HAMILTON OPERATES A TALC MINE IN PENHORWOOD TOWNSHIP AND A MILL AT TIMMINS IN NORTHERN ONTARIO. STEETLEY PRODUCES A RANGE OF MICRONIZED TALC PRODUCTS AVERAGING 2 TO 6 MICRONS IN PARTICLE DIAMETER. THE TALC IS MORE THAN 99 PERCENT PURE PLATEY HYDROUS MAGNESIUM SILICATE TALC MINERAL. IT IS A FUNCTIONAL FILLER FOR PLASTICS ESPECIALLY POLYPROPYLENE, AND FOR TOILETRY APPLICATIONS WHERE IT REPLACES A NUMBER OF FORMERLY IMPORTED TALCS. ANOTHER MAJOR USE FOR THE TALC IS IN PULP AND PAPER MANUFACTURE FOR PITCH CONTROL. THE STEETLEY TALC IS NOTED FOR ITS EXCEPTIONALLY HIGH DRY BRIGHTNESS OF OVER 90 ON THE G.E. SCALE. INDICATED CURRENT ANNUAL CAPACITY IS 25,000 TONNES OF TALC PRODUCTS.

THERE IS EVERY INDICATION BOTH THESE COMPANIES WILL TAKE ADVANTAGE OF ALL MARKET OPPORTUNITIES THAT APPEAR. WITH U.S. PRODUCTION OF TALC IN 1980 ESTIMATED AT 700,000 TONNES FOR PAPER, PLASTIC, PAINT AND OTHER APPLICATIONS A SIGNIFICANT MARKETING OPPORTUNITY APPEARS TO EXIST.

DOLOMITE AND LIMESTONE

A RELATIVELY NEW TREND THAT HAS BEEN IDENTIFIED IS FOR PRODUCERS OF DOLOMITE AND LIMESTONE AGGREGATES TO MAKE FINE GROUND PRODUCTS FOR CARPET-BACKING AND OTHER APPLICATIONS WHERE WHITE COLOUR IS NOT CRITICAL. THE ULTIMATE EFFECT IS A REDUCTION OF MARKETS FOR WHITE CALCITE AND A BROADENING OF OPPORTUNITY FOR FILLERS AT LOWER COST. SEVERAL ONTARIO PRODUCERS HAVE OFFERED FILLERS FOR ASPHALTIC COMPOUNDS SUCH AS ROADS, ROOFING,AND SEALING COMPOUNDS FOR MANY YEARS BUT NOW ARE MOVING TO SUPPLY OTHER MANUFACTURERS. DOMTAR INC., BEACHVILIME LIMITED, OWEN SOUND DOLOMITE, DIVISION OF McASPHALT INDUSTRIES LIMITED AND STEETLEY INDUSTRIES LIMITED ARE ALL ACTIVE SUPPLIERS.

SILICA

INDUSMIN LIMITED IS THE ONLY PRODUCER OF HIGH QUALITY SILICA SUITABLE FOR FILLER APPLICATIONS. BOTH NEPHELINE SYENITE AND MIDLAND SILICA ARE USED FOR HOUSEHOLD CLEANSERS. NO PRODUCTS COMPARABLE TO THE ULTRA-FINE SILICAS OF VARIOUS AMERICAN COMPANIES ARE YET PRODUCED IN ONTARIO.

THE LARGE QUANTITIES OF ALL TYPES OF SILICA IMPORTED INTO CANADA ANNUALLY, PARTICULARLY INTO ONTARIO AND QUEBEC HAVE,RESULTED IN WIDESPREAD EXPLORATION FOR APPROPRIATE DEPOSITS TO SERVE AS MANY MARKETS AS POSSIBLE. IT IS TO BE HOPED THAT EXISTING PRODUCERS WILL CONSIDER THE WIDE RANGE OF OPTIONS OPEN TO THEM INCLUDING FILLERS AND EXTENDERS.

BARITE

HIGH QUALITY DRY-GROUND WHITE BARITE IS PRODUCED BY EXTENDER MINERALS OF CANADA LTD. AT ITS MINE AND MILL NEAR MATACHEWAN IN NORTHEASTERN ONTARIO. THE COMPANY COMMENCED PRODUCTION IN 1974 FROM ONE OF ITS MANY VEIN DEPOSITS AND SUPPLIES GROUND BARITE FOR FILLER AND EXTENDER PIGMENT APPLICATIONS IN PAINTS AND PLASTICS. THE ESTIMATED VALUE OF PRODUCTION IN 1980 WAS $750,000.

MANY BARITE VEINS HAVE BEEN DISCOVERED IN EASTERN ONTARIO AS WELL AS NORTHWESTERN ONTARIO THAT WOULD BE SUITED BY COLOUR AT LEAST FOR FILLERS AND EXTENDERS. HOWEVER ALL THOSE FOUND TO DATE SEEM TO BE RATHER RESTRICTED IN SIZE.

HEDMANITE

HEDMAN MINES LIMITED HAS PRODUCED FINELY GROUND SERPENTINITE MINERAL FILLER NEAR MATHESON SINCE 1969. THE GRAY COLOURED SERPENTINITE IS USED AS AN INSECTICIDE EXTENDER, IN PHENOLIC RESINS, IN REFRACTORY HOT-TOPS AND IN WOOD PRESERVATIVES.

TREMOLITE

RAM PETROLEUMS LIMITED HAS A LARGE DEPOSIT OF TREMOLITE (HYDROUS CALCIUM MAGNESIUM SILICATE) IN PALMERSTON TOWNSHIP IN EASTERN ONTARIO. CONSTRUCTION OF A MILL IS NEARLY COMPLETE TO PRODUCE MICRON-SIZED PRODUCTS INTENDED AS REINFORCEMENT FOR ASPHALT AND OTHER APPLICATIONS.

CHLORITE

IN CARGILL TOWNSHIP, ASSOCIATED WITH THE APATITE CARBONATITE COMPLEX AROUND THE RIM, SHERRITT GORDON HAS IDENTIFIED A LARGE MASS OF VERY FINE-GRAINED, DARK GREEN UNCTUOUS CHLORITE. PERHAPS FILLER APPLICATIONS CAN BE DEVELOPED FOR THIS MINERAL.

ONTARIO GOVERNMENT PROGRAMS TO ASSIST INDUSTRIAL MINERAL DEVELOPMENT.

THE ONTARIO GOVERNMENT HAS ALWAYS ENCOURAGED INDUSTRIAL MINERAL DEVELOPMENT BY PROVIDING GEOLOGICAL INFORMATION THAT RESULTED IN MINERAL DISCOVERIES AND BY PROVIDING SUITABLE INFRASTRUCTURE SUCH AS ROADS AND POWER. THE SERIES OF INDUSTRIAL MINERAL REPORTS DATING FROM THE 1950's TO THE EARLY 1970's PREPARED BY THE ONTARIO GEOLOGICAL SURVEY DID MUCH TO HIGHLIGHT ONTARIO'S INDUSTRIAL MINERAL RESOURCE BASE. MORE RECENTLY THE GOVERNMENT HAS CONCENTRATED ITS EFFORTS ON SELECTED MINERALS AND AREAS THAT SHOW SPECIAL PROMISE OF BEING DEVELOPED IN THE NEAR TERM.

THIS WORK IS IN ADDITION AND COMPLEMENTARY TO THE EXTENSIVE WORK CARRIED OUT BY CANMET, THE ONTARIO RESEARCH FOUNDATION, AND PRIVATE ORGANIZATIONS TO ENHANCE OUR KNOWLEDGE AND PRODUCTION OF INDUSTRIAL MINERALS.

THE ONTARIO GEOLOGICAL SURVEY AND ONTARIO REGIONAL MINES STAFFS HAVE COMPLETED RECENTLY A NUMBER OF STUDIES DESIGNED TO ENCOURAGE ECONOMIC EVALUATION OF INDUSTRIAL MINERALS, MANY OF WHICH WOULD BE SUITABLE AS FILLERS AND EXTENDERS. GEOLOGISTS OF THE EASTERN

REGION OF ONTARIO AND THE ONTARIO GEOLOGICAL SURVEY HAVE BEEN EXAMINING THE GRENVILLE MARBLES FOR THE PAST THREE YEARS TRYING TO UNRAVEL THE COMPLEX SEDIMENTARY HISTORY IN HOPES OF IDENTIFYING A PURE CALCIUM CARBONATE. A REVIEW OF TALC OCCURRENCES WAS COMPLETED EARLY IN 1981. AN ON-GOING STUDY OF SILICA DEPOSITS IN THE EASTERN REGION SHOWS PROMISE OF LOCATING MINEABLE DEPOSITS OF POTSDAM SANDSTONE.

THE ALGONQUIN REGION HAS UNDERTAKEN A LITERATURE REVIEW TO BE FOLLOWED BY LIMITED FIELD WORK OF ALL INDUSTRIAL MINERAL OCCURRENCES IN THE REGION WHICH IT IS HOPED WILL ENCOURAGE FURTHER INVESTIGATION BY INDUSTRY.

THE ONTARIO GEOLOGICAL SURVEY AND THE REGIONAL MINES CO-ORDINATORS OF THE OTHER 6 REGIONS IN THE PROVINCE RECOGNIZE THE INDUSTRIAL MINERAL POTENTIAL AND ARE CARRYING OUT RELEVANT STUDIES.

A STUDY OF FILLER AND EXTENDER APPLICATIONS FOR BARITE, CALCITE, DOLOMITE, KAOLIN, MICA, SILICA, AND TALC IS CURRENTLY UNDERWAY FOR THE MINISTRY OF NATURAL RESOURCES. A SMALL PILOT STUDY HAS RECENTLY BEEN AWARDED TO DETERMINE IF PURE MAGNESIA CAN BE MADE FROM NORTHERN ONTARIO MAGNESITES. WE ARE TRYING TO FIND OUT AS MUCH AS WE CAN ABOUT THE PROVINCE'S INDUSTRIAL MINERALS AND WHAT NEEDS TO BE DONE TO ENCOURAGE MORE DEVELOPMENT. UNQUESTIONABLY FILLER AND EXTENDER APPLICATIONS ARE IMPORTANT ADJUNCTS TO ANY STUDY OF MINERAL RESOURCES.

ONTARIO HAS TWO CURRENT FINANCIAL PROGRAMS THAT ASSIST INDUSTRIAL MINERAL DEVELOPMENT. THE FIRST IS 'OMEP', THE ONTARIO MINERAL EXPLORATION PROGRAM THAT WILL ASSIST THROUGH GRANTS MADE FOR MINERAL EXPLORATION. THE SECOND IS 'BILD', THE BOARD OF INDUSTRIAL LEADERSHIP AND DEVELOPMENT WHICH, WILL CONSIDER APPLICATIONS FOR GRANTS FOR NEW INDUSTRIAL MINERAL CAPITAL INVESTMENT.

THE PROBLEMS AND THE OPPORTUNITIES

DISTANCE FROM MAJOR MARKETS IS THE MAIN PROBLEM FACING ONTARIO PRODUCERS OF INDUSTRIAL MINERALS. BEING 'BIG' IS NOT THE ONLY KEY TO SUCCESS THESE DAYS AS WE ARE FINALLY LEARNING THE HARD WAY. BEING 'OPTIMUM' IS UNDOUBTEDLY A BETTER WAY TO DESCRIBE THE CRITERIA FOR MEETING TODAY'S MARKET CHALLENGES. SOME ONTARIO PRODUCERS WILL CHOOSE TO MEET THE DEMANDS OF THE WIDEST POSSIBLE MARKETS WHILE OTHERS WILL CHOOSE TO SERVE THE MUCH SMALLER MARKETS IN ONTARIO AND OTHER PROVINCES, EVEN PERHAPS CHOOSING TO SERVE ONLY A FEW OF THE INDUSTRIES AND COMPANIES NEEDING MINERAL FILLERS AND EXTENDERS.

RAPID CHANGES IN TRANSPORTATION RATES AND THE POOR SERVICE AVAILABLE FROM MANY NORTH AMERICAN RAILROADS CREATE BOTH DIFFICULTIES AND OPPORTUNITIES FOR ONTARIO COMPANIES. ON THE ONE HAND IT IS BECOMING MORE DIFFICULT TO SERVE CUSTOMERS WELL BY RAIL AT DISTANT POINTS IN NORTH AMERICA. ON THE OTHER HAND IT BECOMES POSSIBLE TO SERVE DOMESTIC COMPANIES BETTER THAN FOREIGN COMPETITORS CAN.

THERE IS A STRONG INCLINATION ON THE PART OF INDUSTRIAL MINERAL PRODUCERS TO SUPPLY THEIR PRODUCTS AT PRICES JUST BELOW THE DELIVERED COST OF REMOTE SUPPLIER'S PRODUCTS, NOTWITHSTANDING THE FACT THE LOCAL PRODUCER'S COSTS MAY BE MUCH LOWER. WE MUST RECOGNIZE THE RISKS INHERENT IN THIS PRACTICE AND HELP OUR MANUFACTURERS TO REMAIN COMPETITIVE ON WORLD MARKETS BY SUPPLYING THEM WITH THE LOWEST COST MINERALS POSSIBLE.

SUMMARY

ONTARIO POSSESSES A WIDE VARIETY OF INDUSTRIAL MINERALS SUITABLE FOR FILLER AND EXTENDER APPLICATIONS. THE 1980'S ARE BRINGING RAPID CHANGES TO INDUSTRIAL MINERAL PRODUCERS AND OPPORTUNITIES TO SERVE NEW NEEDS OF MANUFACTURERS WITHIN REACH OF ONTARIO'S MINERALS. WE EXPECT TO SEE EXPANSION OF EXISTING OPERATIONS AS WELL AS NEW PRODUCTS AND THE EMERGENCE OF NEW PRODUCERS TO SUPPLY THE MINERAL NEEDS OF DOMESTIC AND FOREIGN MANUFACTURERS.

D.G. MINNES
OCTOBER 19, 1981

ONTARIO RESEARCH FOUNDATION

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CLAY AS FILLERS

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CLAYS AS A FILLER - A REVIEW

The term "clay" is generally used to describe one of nature's most abundant non-metallic minerals. However, it should be recognized that it is a term which covers a multitude of materials which vary in colour from red to yellow to brown to white and to black and a wide variety of intermittent shades. They may also vary in their physical form from soft, sticky plastic masses to highly consolidated, hard, slate-like formations (shales).

Clays find a multitude of uses in modern industrial technology, the most well known being those in Ceramics where they act as not only the prime structural components but also as a pigment and a binder. Such products find applications which range from conventional bricks and pottery to high temperature-resistant refractories and highly sophisticated electronic and specialty components.

In recent years, however, the traditional ceramics market for prepared clays has been supplanted by its use as a filler/extender material. Such applications make use of the platey crystal structure, natural binding action, high reflectivity and opacifying properties. In addition, the common occurrence of clay minerals ensures that they are relatively inexpensive which, although it is not a technical requirement, it is often considered to be highly desirable.

It should perhaps be noted at this time that clays do not only find use in a natural 'refined' form for filler applications but also as a harder, more abrasive calcined product.

Despite their common occurrence, however, clays are not universally acceptable as a 'filler' material, the flexibility to produce a variety of coloured products dictates that any filler or extender be of a neutral colour and readily compatible with standard pigmenting procedures. Thus, all of the highly coloured clays (reds, yellows, blacks) are generally discounted from filler applications and only the white (china clay or kaolins) find wide use. Occasionally some of the gray and light brown clays also find application in products where colour is considered non-critical.

Kaolin, (or china clay) is probably the nearest thing to a universal filler, finding major applications in each of the following major manufacturing industries:

- Paper
- Paint
- Plastics
- Rubber
- Agricultural Products - e.g. pesticides and cattle feed
- Chemicals
- Pharmaceuticals

The first five of which are major consumers.

Paper Applications

The application of kaolin clay in paper manufacture is well known and it is reported that approximately 75% of all of the china clay produced is used for the manufacture of paper and board. The very best grades, i.e. those which exhibit brightness (reflectance) values of ∿95% to 97% are used for high quality paper coating in fine paper, the slightly lower grades with brightness values of about 90% to 95% are used as paper fillers.

The high brightness, inertness and particle shape of kaolin-clay make it highly suitable for filling the interstices of the cellulose fibres which are the major components of paper. High retention in the paper sheet during the manufacturing process is also a prime requisite, and kaolin clay readily meets this requirement. The presence of clay as a filler in the paper sheet increases its opacity and improves the printing characteristics of the surface. The amount of clay used as filler depends upon the type and grade of paper being manufactured but may typically contain up to 30% by weight for a good quality product.

Publications on this topic are numerous and the specifics of clay utilization by the paper industry has become a major science in itself. Reference should be made to the several publications of TAPPI (The Technical Association of the Pulp and Paper Industry) for more detailed specifications.

Paint Applications

The main constituents of paint are:

- Binder (vehicle)
- Solvent and,
- Pigment

together with specific additives such as fungicides, and dispersants, etc. The pigment component comprises of the prime colouring pigment plus an inorganic extender.

The physical and chemical properties of kaolin clay make it ideally suited for use as an extender; it is readily dispersed, is very slow to settle out, it imparts smooth flow properties and the flat platey particles help to develop opacity.

The function of the extender in the early days was to increase the solids content and reduce the cost of the paint with an inexpensive, white, chemically inert product. It is now considered, however, that the extender can impart distinct advantages to the paint and the correct choice of such a material is important in determining optimum performance. The total quantity of extender which can be incorporated into the paint is determined by the end-use properties desired.

For example, significant changes in paint film properties occur in certain common regions of volume concentration (known as the critical volume concentration). In the case of a gloss paint, it should contain a low volume of pigment or extender (i.e. below the critical volume concentration). However, as the proportion of the extender is increased above this level, the gloss will disappear and a matte film will be produced instead. Obviously the covering power would be minimal at low levels of extender and would improve as the proportion of extender increased. Other properties such as durability, resistance to abrasion and surface appearance are also influenced by the proportion of extender contained in the formulation.

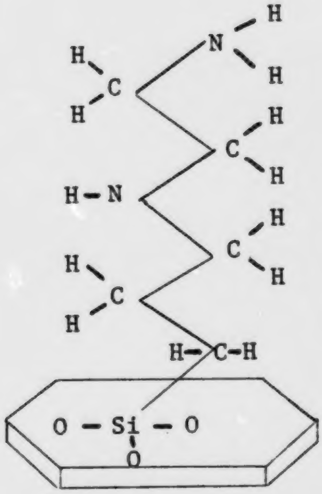
Extenders of different shapes and sizes have different effects on paint film properties, for example, more equi-dimensional-shaped particles such as ground calcium carbonate tend to give less opacity than kaolin but improved gloss characteristics and finer fractions of kaolin clay will result in greater opacity and whiteness than an equivalent volume of a coarser-grade clay.

Rubber Applications

There are a number of articles made from rubber products such as shoe soles, rubber boots, tennis balls, rubber mats, gaskets, cable insulations and carpet backing which may all contain clay or other minerals as fillers.

Fillers in this industry can be categorized by the effect that their physical properties have on those of the rubber compound - hard or reinforcing fillers are usually of fine particle size - soft fillers are usually less fine - the choice of filler being determined by the end use properties of the rubber. (See "Fillers in Rubbers" by D.A. McKillop - Dunlop).

One very interesting advantage of kaolin clays as potential reinforcement in elastomers is its ability to be modified by the addition of Amino Silanes. The quality of pigment reinforcement in elastomers is, to a high degree, dependent on the ability of the pigment to interact chemically with the polymer, forming pigment to polymer bonds; such a modification with Amino Silanes (as shown schematically below) results in significant improvements in modulus, abrasion resistance and many other properties in a wide range of products.



Schematic Representation of Amino Silane Modified Kaolin

Plastics Applications

In the field of plastics, of the many items which can be fabricated from plastics, not all use mineral fillers. However, as oil prices increase, the pressure increases on plastic producers to reduce costs, therefore a high degree of research is currently in progress to find suitable fillers.

The use of clays for such applications appears to be in its infancy at this time, however, at the outset, clays appear to be a natural candidate as a filler due to their thin platey nature, and naturally occurring fine particle size (as shown in Figures 1 and 2).

One interesting use where clay is used as a filler in plastics because of its specific physical properties is plastic cable insulation where a calcined clay is used to give high electrical resistance and abrasion resistant properties. It is interesting to note that such a calcined product is no longer the soft platey material but a more angular abrasive material.

The trend to more plastic components in the automobile industry is seen as a possible boost to the potential use of clays as a plastic filler.

Agricultural Applications

The agricultural industry utilizes clays and other industrial minerals as binders, extenders and diluents in both fertilizer and animal feedstuffs.

One of the major problems experienced with granular fertilizers is that they tend to cake and stick together upon compaction and storage, causing severe handling and application problems in the field. This is particularly serious for those fertilizers bearing high nitrogen levels.

Kaolin clays (sometimes modified with an amine coating) and other minerals such as talc are used to prevent further agglomeration of the granules.

Clays can also be used as inert carriers for agricultural insecticides, pesticides and weed killers where they are a means of transporting the active chemical ingredient and releasing it at a controlled rate.

There are many different applications for an inert non-toxic mineral in animal feed compounds. Typically, animal feed cubes and pellets are roughly handled during transportation and storage, whether it be in silos or bags, and thus much wastage may occur. Clays have been included in feed compounds to strengthen cubes and pellets and prevent such breakdown. The clay not only acts as a binder but also as a filler.

Interestingly, it has been reported that research in the U.S.A. has shown that chickens fed on diets containing clay put on weight quicker and laid more eggs. It has been postulated that the clays form thixotropic gels in the stomachs of the chickens and retard the natural passage of food allowing time for more useful protein to be extracted.

Miscellaneous Other Chemical Applications

Many pharmaceuticals contain highly refined kaolin clay. The material is completely bland and harmless when taken internally and the soft powder makes an ideal carrier and binder for the active ingredients.

Certain qualities of wallpaper make use of a ground coating of kaolin which is applied to aid in the reproduction of the printed designs.

Some fine quality leathers are dressed with a preparation containing kaolin clay. The material fills the pores and helps to produce a smooth textured surface.

Kaolin clays are often used in the textile industry as a component of a preparation used to strengthen fibres during wearing.

Canadian Clays

At this point in time, there appear to be no Canadian clays. Finding commercial application as fillers, kaolin clays are imported from both Europe and the southern states of the U.S.A. in volumes which are sufficiently large and lucrative to encourage producers of other industrial minerals to actively pursue R & D programs aimed at substituting other materials for the clay.

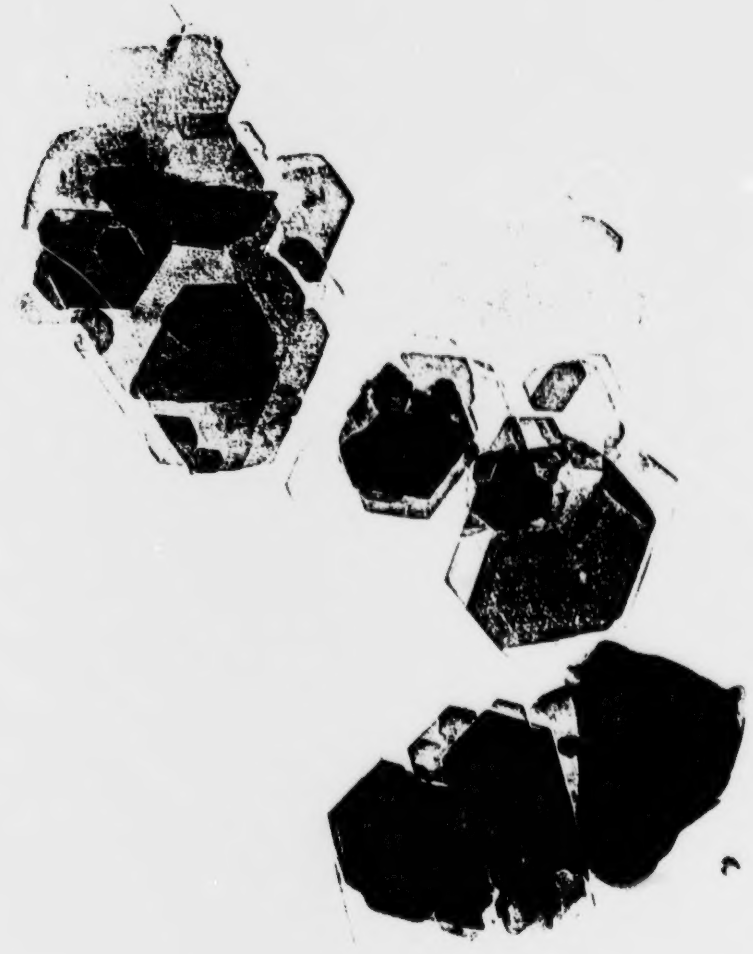
This does not mean that Canada does not possess useable clay deposits, although it should be noted that the higher-quality materials are located in areas which are currently well-removed from urban areas.

Of the deposits which are currently being exploited, there are several clay and shale quarries being worked by the heavy clay products industry, and one of these, located in Mississauga, Ontario, currently produces a bagged, air-floated product which is light-gray in colour and which could possibly find application as a filler where colour is not a critical property.

There are several kaolin clay deposits in Canada, the most notable of which are in Quebec, Ontario and Saskatchewan and none of which are currently being exploited. Probably the best known of these deposits are the Ontario kaolins of the James Bay Lowlands; this deposit (located north of the Trans-Canada Highway) appears to be extremely large, outcropping in several places, and consists of a mixture of kaolin clay and silica sand in a ratio of approximately 1 to 6, respectively.

The kaolin fraction appears to be very fine and well crystallized as shown in the transmission electron micrograph in Figure 1. The crystals compare well with similar micrographs of a high grade U.S.A. kaolin clay shown in Figure 2. The materials have been evaluated for various filler applications with encouraging results. Although additional beneficiation is required to upgrade the clay to the standards of currently imported products, the location has thus far been a major factor in their lack of development. However, it is considered that if prices of imported kaolin clays continue to rise, the viability of the Canadian deposits will improve significantly.

Figure 1



A Transmission Electron Micrograph of a Kaolin Clay Sample

Obtained from the James Bay Lowlands, Ontario

Figure 2

A Transmission Electron Micrograph of a High-Grade Kaolin Clay

From a U.S.A. Source

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MICA AS FILLERS

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Mica as Fillers

ORF/CANMET Minerals Fillers Seminar

I. Introduction

Mica is a unique mineral. Unlike asbestos that is fibrous, and wollastonite that is needle-like, it is a glassy, very thin flake (in effect a natural glass) differing in dimensions from other platey minerals such as talc. This characteristic of mica, along with its general inert character, makes it potentially valuable for inclusion in matrices. Mica, having been delaminated into individual flakes, tends to overlap and form a "fish-scale" effect useful in heat-shield or corrosion resistant applications. It has some lubricity in the flat plane, but tends to be a stubborn friction material in the edge plane. This suggests its possibility as a component for brake linings. Further, when mica is encapsulated in plastics, the platelets tend to line up in one direction to make it very stiff. These properties of mica, along with electrical and thermal insulating values, suggest that it can be used in a number of materials.

There are generally three kinds of micas found in North America. They are: most commonly, muscovite mica; and sericite; and, most infrequently, phlogopite micas. Muscovite micas occur in wide deposits, usually occurring as pegmatities, and are mined in copious quantities in the south-eastern United States, principally in North Carolina and Alabama. They have occurred in the south west, New Mexico and Arizona, in the north east in Pennsylvania, New York, and Connecticut and in some of the north western states. Very frequently, muscovites occur in low proportions with clay and silica and are associated with other minerals such as feldspar and spogamine. The sericites are, to a large degree, impure, weathered minerals containing a low percentage of mica and a high percentage of silica. The phlogopite, of which Suzorite mica is the most notable example in North America, has been found in eastern Canada in many locations. The Suzorite deposit is very unusual in that it is very high purity, high concentration and large volume. The Marietta Resources - Laviolette deposit, located in south central Quebec, is a very extensive, homogenous ore body that has been core drilled and identified at +30,000,000 tons. Phlogopites also occur in Ontario and other provinces but have not been reported in deposits as large or in high concentration.

There are, of course, different properties associated with every ore body, regardless of the type of mica, that result from the original formation of the deposit the result from variations in chemical composition. A general difference between phlogopites and muscovites, as shown on the chart below, is that the muscovite, containing very little iron in the molecular structure, tends to be a silvery white material of small particle size with accompanying clay and silica minerals. Suzorite mica is brown or golden, is of larger flake size and is higher temperature resistant.

Table attached.

Chemical composition of pure Suzorite mical flake

Component	Per cent by weight
SiO_2	40.7
Al_2O_3	15.8
MgO	20.6
K_2O	10.0
Total Fe (as FeO)	8.9
F	2.2
H_2O+	3.0
BaO	0.5
Na_2O	0.5
TiO_2	0.4
Cr_2O_3	0.2
NiO	0.3
V_2O_5	0.1
S and P	0.1

Physical properties of pur Suzorite mica flake

General properties		Bulk density (Scott volumeter)	9-40 pcf (145-64 kg/m^3), depending on grade
Color	Amber brown		
Shape	Thin Flakes		
Particle nominal diameter	20 microns to 0.25 inch (0.64 cm), depending on grade	Specific gravity	2.9
		Hardness	2.5-3.0
		pH (of aqueous suspension)	7.5
Particle thickness	0.5 to 300 microns, pending on grade	Water solubility	Virtually insolubl

(continued on other side)

Suzorite® mica

Physical properties of pure Suzorite® mica flake (continued)

Mechanical properties

Tensile strength (calculated)[*]	125 x 10^3 psi (860 MPa)
Modulus of elasticity[**]	25 x 10^6 psi (172 GPa)

Electrical properties

Dielectric constant (100 Hz)[†]	6—6.7
Dissipation factor, tan δ (100 Hz)[†]	4.5—8.2 x 10^{-2}
Volume resistivity[††]	7.5—8.8 x 10^{10} ohm-cm

Optical properties—radiation absorption

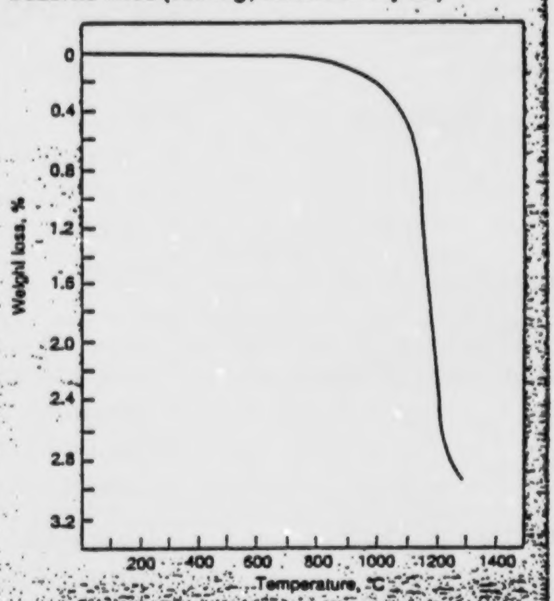
Refractive index	1.598
UV, visible absorption[§]	Low transmittance (35—40%) in 600—800 nm visible region. Very strong absorption in 200—400 nm UV region.
IR absorption[§]	Very strong absorption above 9 microns
Microwave absorption (at 2450 MHz):	
Temperature increase	0.03°F lb/sec kw (6.8°C g/sec kw)

Thermal properties

Coefficient of thermal expansion[#]	
—perpendicular to cleavage plane	9 x 10^{-6} K^{-1}
—parallel to cleavage plane	4 x 10^{-6} K^{-1}
Maximum temperature with little or no decomposition	1000°C

Suzorite mica has outstanding thermal stability over a broad temperature range, significant in high-temperature processing and operation—e.g., hot topping in foundry work, glass-bonded and phosphate-bonded mica, and as a replacement for asbestos in fire-resistant boards and friction materials. As the thermogravimetric analysis (TGA curve) below shows, even at 1000°C, the weight loss of Suzorite mica is lower than 0.4%.

Thermogravimetric analysis of -20+40 mesh Suzorite mica (350 mg, heated in dry air)



Weight loss of Suzorite mica, muscovite mica, and chrysotile asbestos after exposure to heat for 60 minutes:

	600°C	900°C
Suzorite mica (-100+200 mesh)	0.11%	0.26%
Muscovite (-100+200 mesh)	3.4	4.2
Chrysotile (4T-3)	12.1	13.9

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[*] *J. Mater. Sci.*, 8, 1373 (1973)

[**] U.S. Bu. Mines Bulletin 647

[†] Measured on single large flake (ASTM D-150)

[††] Measured on single large flake (ASTM D-257)

[§] Measured on 0.04-mm-thick single large flake

[#] X-ray diffraction powder method

Suzorite® mica

	Suzorite®	U.S. Muscovites
Color Flakes	Golden to brown	Pure white
Sizes Available	1/4" to −325 mesh	−40 to −325 mesh
Process	Dry ground	Dry or wet ground
Grades Produced	3 crude 5 pure mica 4 fluid energy 4 coated	2 crude 2 pure mica 2 fluid energy None
Temperature Limits	2700°F	2200°F
Markets	7	4
Added Value Programs	4 coupling agents 1 intermediate compound 1 plastic compound 1 finished product	none none none none
Price Range ($US)	$130–570	$70–280
Reserves (tons)	30,000,000	by-product mostly

5/

The key differences between the two materials, which tend to guide its end-use to some degree are as follows:

1. Color

Muscovite mica, being silvery white, is preferred for pigment substitutions and decorative purposes for lightly pigmented decorative paints, wallpaper and cosmetics. This could also be a factor where the mica is contributing luminescence, or whiteness, to the end product.

Suzorite mica, with its characteristic gold color, can be used where such pigmentation or decorative purposes are required. It has been used in plastics and insulating materials to take advantage of its distinct color.

2. Temperature Difference

Suzorite mica, a phlogopite, is resistant to higher temperatures than muscovite. The difference of a few hundred degrees may not be significant for some end uses, but it can be important in many applications. These properties are also important where the molding temperatures of materials may be sufficiently high to cause flake breakdown in the matrix.

3. Strength

It is characteristic of Suzorite mica to normally have a higher flex strength than most muscovites. Since this rigidizing property is a very critical one provided by mica in composites, the fact of having additional strength would be of value to the end user.

4. Purity

There are two factors here. Many of the muscovites sold in North America are produced from the by-products of other minerals, such as feldspar, and tend to contain additional minerals in the base ore deposit. These materials include clay and silica that are frequently the same light color as muscovite mica, but do not provide the same physical characteristics as mica.

Suzorite mica is prepared from an ore body that begins at 85% pure and contains virtually no silica and no clay or asbestiform materials. This higher purity is of value where the physical properties of the mica are sought by the end user.

II. Analysis of Markets

In the development of the Suzorite mica mineral venture, it was recognized that most traditional markets for mica have employed this material as a "commodity". In this market, there had been virtually no expansion or growth in the previous ten years. The Marietta Resources International-Laviolette marketing interest was not to enter a commodity or traditional market, but to develop products that would take advantage of the unique nature of the mineral. Several years' product development, research, and communications with potential user industries were undertaken. A number of products were attempted and rejected, or deferred. A number of materials appeared to be economically unattractive. After an extensive program of selection and rejection it became evident that mica, and particularly phlogopite mica, had important virtues as a reinforcement or supplementary material in a number of product areas.

Physical properties of mica tend to make it very valuable to use in place of, or along with, other materials that are higher-priced or of less valuable characteristics. Mica being inert, strong, heat resistant, stiff, benign and characterized by a crystal uni-planar strong structure, relatively smooth and slippery, that has enabled mica to find a place as an additive in many industrial products where the design component or unique properties of mica were needed.

The best examples of these properties is that mica has been added to gypsum board joint cement to provide trowelability, smooth finish, resistance to heat and cracking. Mica is used in building materials because of its inert nature and heat reflection ability. Following a search for products needing special properties, MRI looked for future markets that had a high degree of engineering required, potential for growth, and potential for added value, both to the product and to its price.

A brief description of each of these markets follows:

A. Joint Cement

Micas have been traditionally used to provide properties described above. Growth has expanded as asbestos has been reduced in the formulation, also the dry wall industry has grown as a general case. This is a relatively active market in the United States and Canada and is beginning to develop worldwide.

B. Oil Well Drilling Fluids

Micas has been employed as one of the 25 or 30 ingredients used for oil well drilling fluids and provides its own special characteristic. Just as clays and barites provide lubricity and resistance to pressure, so mica is used to seal cracks in lost circulation zones and reduce the loss of high-priced composite fluids.

B. Oil Well Drilling Fluids (continued)

Suzorite mica in its coarse, mostly unrefined state, is marketed into this low price, but high value, end use.

C. Molding Compounds

A third traditional mica market (along with silicones) has been for tire molding where easy parting and lubricity is of value. It is a limited market requiring high quality, well ground material.

C. Asbestos Substitutes

This new technical market promises to be of major proportions and will take advantage of many of the properties in mica. It has been a particularly useful market for Suzorite mica since this mica has a unique chemical composition that gives it certain temperature and physical property advantages over many muscovites.

Where heat resistance properties are valuable, it is useful in insulation and roofing products. Where fire-proofing is of value, it is used structurally for fire-proofing. Where friction materials are called upon, mica has merit in brake linings. In electrical insulating properties, Suzorite mica has found a valuable home.

E. Reinforced Plastics

Another of the more promising growth areas for mica is to join that family of industrial minerals that, along with glass shapes, gives characteristic improvements in reinforced plastics. Special properties unique to mica are provided. It is only needed that the end product requires those specifications.

Below are tables, one of which is from the United States Bureau of Mines, estimated usage of micas for selected years which primarily reflects production of grades of mica for traditional markets. Suzorite mica has been sold in the very limited quantities in these markets.

Tables Attached.

Table 7.—Consumption and stocks of mica splittings in the United States, by source

(Thousand pounds and thousand dollars)

	India		Madagascar		Total[1]	
	Quantity	Value	Quantity	Value	Quantity	Value
Consumption:						
1975	4,625	2,529	120	104	4,746	2,634
1976	4,903	3,084	122	142	5,025	3,226
1977	3,979	2,525	165	193	4,144	2,718
1978	5,371	2,837	166	194	5,537	3,031
1979	4,714	2,745	163	503	4,877	3,248
Stocks on Dec. 31:						
1975	3,465	NA	44	NA	3,510	NA
1976	3,166	NA	124	NA	3,290	NA
1977	3,130	NA	68	NA	3,198	NA
1978	2,696	NA	78	NA	2,771	NA
1979	2,331	NA	110	NA	2,441	NA

NA Not available.

[1] Data may not add to totals shown because of independent rounding.

Table 8.—Built-up mica[1] sold or used in the United States, by product

(Thousand pounds and thousand dollars)

Product	1977		1978		1979	
	Quantity	Value	Quantity	Value	Quantity	Value
Molding plate	1,227	2,751	1,439	3,062	1,549	3,951
Segment plate	1,406	3,787	1,558	3,892	1,558	4,423
Heater plate	172	249	165	329	168	485
Flexible (cold)	617	1,904	577	1,914	634	2,276
Tape	775	3,414	878	3,018	744	2,721
Other	346	1,246	324	1,301	402	1,801
Total[2]	4,545	13,351	4,941	13,516	5,055	15,657

[1] Consists of alternate layers of binder and irregularly arranged and partly overlapped splittings.

[2] Data may not add to totals shown because of independent rounding.

Table 9.—Ground mica sold or used by producers in the United States, by end use

(Thousand short tons and thousand dollars)

Use	1977		1978		1979	
	Quantity	Value	Quantity	Value	Quantity	Value
Roofing	3	200	7	635	W	W
Rubber	5	1,202	4	1,044	4	1,177
Paint	25	2,703	21	2,367	19	2,233
Joint cement	57	4,481	58	4,898	63	6,315
Other uses[1]	32	3,320	34	4,034	36	4,796
Total[2]	122	11,906	124	12,979	122	14,522
Brick and other[3]	41	291	40	164	40	179

W Withheld to avoid disclosing company proprietary data; included with "Other uses."

[1] Includes mica used for agricultural products, molded electric insulation, plastics, welding rods, well drilling, textile and decorative coating, wallpaper, and uses indicated by symbol W.

[2] Data may not add to totals shown because of independent rounding.

[3] Low-quality sericite.

Canadian mineral imports

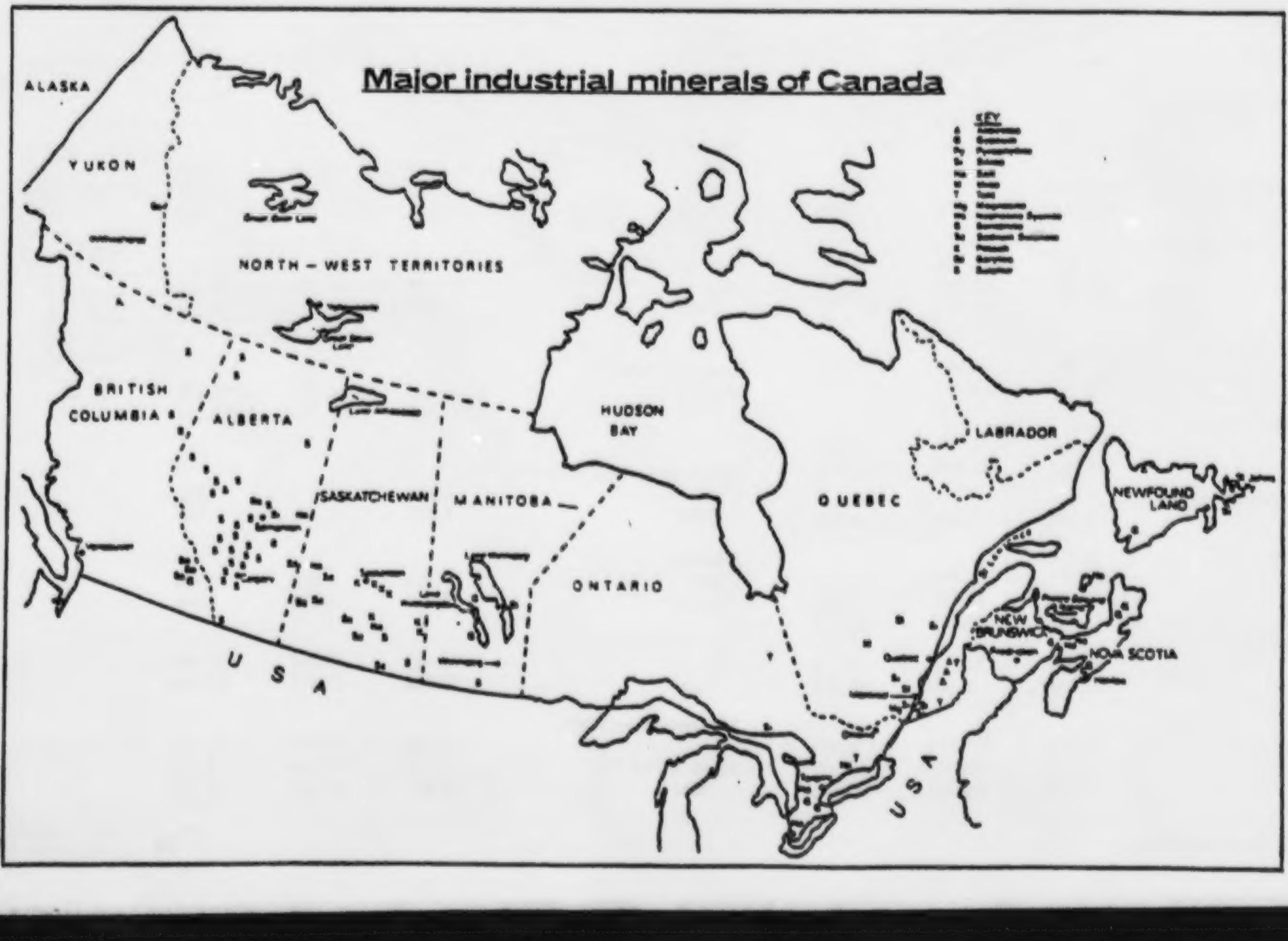
(Short tons, unless specified, only principal countries of origin shown)

	1978	*1979*	*1980*
Abrasives — natural nes (long ton)			
USA	14,742	19,315	11,182
Total	14,886	19,580	11,288
bestos			
South Africa	560	1,219	963
USA	274	884	338
Total	844	2,153	1,274
Barytes			
USA	20,095	9,247	53,487
Total	20,095	9,257	53,737
Bentonite (long ton)			
USA	304,628	467,272	337,529
reece	85,359	208,085	123,938
Total	389,987	675,438	461,872
Cement — clinker (long ton)			
USA	7,713	21,075	439
pan	32,729	38,239	49
Total	40,562	59,512	488
Portland cement (long ton)			
SA	107,859	121,828	121,849
Total	109,542	121,960	122,146
Cement — other (long ton)			
USA	129,279	90,403	86,550
Total	132,883	92,365	88,755
China clay (long ton)			
USA	172,693	254,904	219,362
nited Kingdom	27,799	46,469	30,971
Total	200,496	301,396	250,333
Fireclay (long ton)			
USA	37,546	57,581	38,364
Total	38,444	57,589	38,713
Clays — others (long ton)			
USA	181,224	130,956	107,403
Total	181,576	131,799	107,830
rude refractory materials nes (long ton)			
Total	25,911	24,374	32,059
iamonds — industrial (carats)			
SA	552,668	832,864	799,098
rish Republic	333,398	365,243	331,604
Total	1,023,583	1,332,418	1,343,395
iamond dust (carat)			
SA	741,469	1,120,694	1,268,705
Total	750,417	1,134,411	1,287,451
Diatomite (long ton)			
SA	27,969	32,646	27,614
Total	27,969	32,646	27,614
Dolomite — calcined (long ton)			
USA & Total	3,204	4,316	4,248
uller's earth			
exico	120,413	116,693	120,111
Morocco	13,733	14,790	43,881
South Africa	32,243	23,155	30,321
United Kingdom	—	—	23,492
USA	10,044	21,168	19,568
Total	187,654	185,083	246,852
ypsum			
exico	64,329	147,874	131,939
USA	13,708	20,011	38,607
Total	78,259	168,062	170,546
Magnesia — dead burned or sintered (long ton)			
USA	52,178	64,500	58,354
W. Germany	8,145	6,502	4,991
Total	68,347	93,620	70,134
Magnesia — other (long ton)			
USA	3,539	4,334	5,256
Total	3,642	4,385	5,256
Mica — blocks, sheets, and ground (long ton)			
USA	33,504	45,300	38,389
Total	34,314	45,723	40,255
Phosphate rock			
USA	3,345,798	3,589,952	4,206,909
Total	3,355,324	3,591,853	4,206,986
Pumice (long ton)			
USA	12,542	22,073	45,000
Greece	—	19,558	—
Total	12,642	41,720	45,138
Salt and brine			
USA	1,080,992	999,512	804,157
Mexico	361,301	374,881	427,359
Spain	23,986	15,592	36,180
Total	1,466,597	1,406,747	1,268,984
Silica sand			
USA	1,352,229	1,819,821	1,297,765
Total	1,369,560	1,820,897	1,304,543
Sand and gravel			
USA	1,995,090	1,310,598	1,328,089
Total	1,996,274	1,324,882	1,331,786
Granite — rough			
South Africa	11,418	16,727	9,896
USA	5,056	6,941	13,119
Total	18,809	24,981	24,130
Marble — rough			
Italy	3,782	6,298	4,496
USA	2,728	3,268	2,778
Total	6,544	9,583.	7,337
Building stone — rough nes			
USA	12,037	11,890	10,114
Total	2,155	1,388	10,284
Crushed limestone			
USA	3,166,619	3,544,524	2,665,410
Total	3,167,603	3,544,721	2,665,543
Silex and crystallised quartz			
USA	2,144	1,368	305
Total	2,155	1,388	309
Sulphur			
USA	8,824	1,860	1,936
Total	8,962	1,873	1,948
Talc or soapstone			
USA	36,486	55,062	55,444
Total	36,762	55,471	55,696
Vermiculite — crude			
USA	35,085	33,257	38,137
South Africa	20,729	8,064	8,550
Total	55,814	41,321	38,137

Industrial mineral producing mines[1] in Canada as of January 1980

Mineral	*Nfld.*	*P.E.I.*	*N.S.*	*N.B.*	*Que.*	*Ont.*	*Man.*	*Sask.*	*Alta.*	*B.C.*	*Y.T.*	*N.W.T.*	*Total*
Asbestos	1				7					1			9
Barite										3			3
Gypsum	1		5	2		3				1			12
Limestone	1		4	5					6	4			18
Magnesitic dolomite			2		1								3
Mica					1								1
Nepheline syenite						2							2
Potash								10					10
Pryophyllite	1												1
Salt			2			2		2	1				7
Silica	1		2	1	6	2	2						14
Sodium sulphate								7	1				8
Talc/soapstone					2	1							3
Titania-iron					1								1
Total industrial mineral value ($ '000)in 1978	33,789	1,901	90,117	47,387	1,041,732	579,838	89,541	555,320	237,893	199,305	32,404	—	2,909,227

[1] Producers of clay products and construction materials not shown.
Source: Provincial and sector mining association data, The Mining Association of Canada.


Major industrial minerals of Canada
KEY
ALASKA
YUKON
NORTH – WEST TERRITORIES
BRITISH COLUMBIA
ALBERTA
SASKATCHEWAN
MANITOBA
HUDSON BAY
ONTARIO
QUEBEC
LABRADOR
NEWFOUND LAND
NEW BRUNSWICK
NOVA SCOTIA
U S A
U S A

	1979		*1980**	
	Tonnes	*C$*	*Tonnes*	*C$*
Industrial minerals				
Asbestos	1,343,329	506,607,118	1,169,000	518,714,000
Titanium slag	—	72,219,178	—	108,300,000
Ilmenite	—	3,438,796	—	4,256,000
Silica	613,091	8,927,703	690,000	11,602,000
Peat	217,171	14,602,073	217,000	14,748,000
Magnesitic dolomite	52,553	8,990,157	53,000	10,405,000
Sulphur	69,595	1,370,130	94,000	1,732,000
Talk & steatite	32,057	1,499,574	30,000	1,306,000
Mica	10,980	1,697,892	10,000	1,851,000
Feldspar	c	c	c	c
Graphite	c	c	c	c
Lime	414,602	19,712,970	375,000	19,703,000
Total (Industrial)		639,065,591		693,147,000
Structural materials				
Stone (granite incl.)	63,250,913	185,072,775	55,359,000	158,572,000
Cement	3,212,241	137,609,617	2,699,000	139,716,000
Sand & gravel	79,576,125	83,784,003	57,916,000	70,274,000
Clay products: Bricks	120,975**	15,445,875	101,605**	15,843,000
Others	—	3,866,595		3,411,000
Total (Structural)		425,778,865		387,916,000
TOTAL (Non-Metallics)		1,064,844,456		1,081,063,000

* *Preliminary figures*
** *Thousand bricks*
c *Confidential data*

which comes in many varieties of superior quality is available in more than twenty-five colours. The production of granite is valued at around $14m. per year.

ONTARIO

Ontario produces many industrial rocks and minerals including, barite, building and ornamental stone, calcite whiting, metallurgical and glass grades of calcite and dolomite, granite, gypsum, nepheline syenite, salt, silica, structural materials (cement, clay and shale products, crushed stone, lime, sand and gravel), serpentine, and talc.

Deposits of asbestos, refractory clays, potash feldspar, fluorspar, kaolin, kyanite, magnesite, marble, muscovite and phlogopite micas, phosphates, spodumene, tremolite, vermiculite, and other industrial rocks and minerals are known.

For further information contact:
Industrial Minerals Section
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Ontario
Ministry of Natural Resources
Hon. Alan W. Pope
Minister
W. T. Foster
Deputy Minister

Peat

The inventoried resources of peat in Quebec amount to about a billion tonnes with a 50% moisture content while the total potential is estimated to be five or six times larger. This large potential and the many uses of peat resulting from its physical chemistry have prompted the Government of Quebec to pay special attention to the development of this commodity. In 1981, C$2m. will be spent in R&D activities through the co-operation of the private and public sectors. These investments will focus on the development of new technologies for the exploitation of peat, the inventory of peat resources, and the investigation of new agricultural, industrial, and energy end uses. The substitution of peat for bentonite in the pelletisation of iron ore and the development of mechanical presses to reduce the moisture content of peat down to 70% at the mine site are among the major projects being carried out.

There are approximately forty peat producers in Quebec. Their production is almost exclusively used for horticultural purposes and nearly 90% of it is exported to the USA. The 217,000 tpa of 50% moisture peat produced in Quebec represent close to 45% of the Canadian production.

Mica

A joint venture between *Marietta Resources International Ltd.* and *Société Minérallurgique Laviolette, Inc.* operating in Quebec is the sole producer of mica in Canada. In 1980 the production of suzorite (a variety of phlogopite mica) reached 10,000 tonnes. Suzorite is sold as a highly delaminated mica treated with various additives according to the market served. Over 60% of the mica is shipped to foreign markets, especially the USA and Japan.

Two other large deposits are held by a Crown Corporation, *SOQUEM* and *Société Koizumi Group (Canada) Ltd.* The known reserves of mica in Quebec exceed 60m. tonnes and rank third in the world. Considerable growth possibilities exist for mica in drilling mud and particularly in deep drilling. The demand for mica should also increase at a fast rate in the plastic industry where it is used as an ideal complementary filler for applications in the automobile, containers, and construction industries.

During the ten years that Marietta Resources and Laviolette have studied the long-range potential for mica in North America and throughout the world, it has been our premise that the relatively static growth of this important industrial mineral (somewhere between 0 and 2% in the late 60's and early 70's) could be expanded to a 4 to 7% growth rate, but only if it is based on developing new products. As part of a rapidly expanding reinforced plastics and asbestos substitute market, it should match the growth of these industries. Their growth has been forecasted by many marketing analysts at 8 to 12% per year. A long-range plan for Suzorite mica is based on market growth of 1 and 2% for traditional markets, and 7 to 9% for the more technically involved products. Production and sales experience in the last two years has supported such long range expectations. Caution must be exercised however -- these products will only be successful if their technical values are established and supported by the producer. In other words, sales growth will not occur unless the technical excellence of mica in each of these products can be established and data transmitted to the decision makers in each of these user industries.

III. PROPERTIES, CHARACTERISTIC EFFECTS

Suzorite mica, as is true of all micas, has several valuable properties that tend to suggest its applications. It is, of course, inert and resistant to many acids and bases; it has value in corrosion resistant and moisture resistant applications. Being resistant to high temperatures and with high electrical resistivity, it provides good insulation from electrical impulses and heat. Thus, mica can be used in roofing products, building materials and electrical insulators. Its flake form permits a certain amount of "fish scaling" so in such matrices as plastics, asphalting materials, and paint vehicles, the flakes will orient themselves in such a way as to create a barrier to moisture and gases. A significant new development has been to use this characteristic in vibration damping where previously very heavy minerals such as barium sulfate or asbestos had been used.

In the reinforcement of plastics, mica behaves in very much the same manner as glass flake and provides stiffness and good flexural strength, resistance to heat distortion, and good molding characteristics. Although mica does not have the characteristics of fiberglass fibers and provides good impact and tensile strength, it can, in combination with such minerals, give superior engineered plastics. The future for mica in reinforced plastics is extremely bright, particularly since its present favorable cost comparison with glass will only improve as the cost of fuels rise that are necessary to produce glass. The technology that will improve bonding between organic materials and such inorganics as mica will offer continual improvements in its performance.

The opprobrium that has been growing against the uses of asbestos where consumers or workmen may be exposed to fibers gives opportunities for mica that were not anticipated many years ago. Although we expect asbestos will continue to be the important unique mineral that it always has been and will be used for purposes that cannot be readily replaced, there is a growing potential for mica as a replacement or supplement in asbestos containing materials.

The potential is enormous. Those applications where mica can supplant asbestos could well exceed several hundred thousand tons per year in North America alone, as well as participating in large markets in western Europe and Japan.

When one considers that asbestos is used in brake shoes, cement building materials, thermal insulation, vibration damping products, fire-proofing materials, gaskets, coatings, and some household products, it becomes evident that mica can become a factor in these products and processes.

In our experience, an early potential has been in fire-proofing, vibration and sound damping. This latter application, not significantly important in years past, grows in significance as the automobile industry looks for smaller vehicles, lower horsepower, and seeks to protect passengers against road and engine noise and vibration.

It has been the experience of our development and marketing groups that mica can often be a supplement or substitute for glass, asbestos, calcium carbonate, barium sulfate, talc and many other products. It, in effect, occupies a place where it is much cheaper than some fillers and reinforcements on one hand; and on the other, may be at a higher price, but provide better performance. It is the prediction of our company that mica, with somewhat higher temperature resistance and other properties that result from its unique chemical composition, can have a specific and significant role, even with some advantages over other micas.

IV. WHAT AND WHO IS "SUZORITE MICA" AND MARIETTA RESOURCES

Since this conference is not intended to discuss information regarding the companies involved, these remarks will be brief. It is useful, however, to understand the context in which mica has been developed by the joint venture of Marietta Resources, a part of Martin Marietta Corporation, and by Laviolette Metallurgical Mineral.

Martin Marietta is a company limited in its diversification to manufacturing materials, mostly produced from minerals. It also includes an important space technology division that has been closely coordinated with the U.S. defense and space efforts. This is important since the research and development that backs such manufacturing can give impetus and creative ideas to the use of mica in new products. Although this has not been a significant effort on the part of the program, it has been important in applications and should grow in the future.

The company's other activities, production of aluminum from the basic ore to the finished metal, stone and aggregates for the building industry, magnesia, cement, and chemical products provide expertise for the mining, processing, marketing, and product development of many of the materials of which mica hopes to play a role.

Martin Marietta created a subsidiary some ten years ago to develop minerals throughout the world and did form, as a consequence of this organization, a joint venture with Laviolette in Quebec. This partnership has been a long, friendly, and close relationship which both companies intend to support and to grow into an operation profitable for both companies as well as Canada and Quebec.

V. COMPARISON OF FILLERS VS. PROPERTY MODIFIERS

The use of mica in fillers here discussed deals only with the marketing categories referred to earlier as an asbestos substitute or supplement and as a reinforcement for plastics. First consider plastics.

I believe we are all aware that in 1979 and 1980 there were approximately 20 million tons of all plastics used in the United States. It is generally the case that between 10% and 20% of the United States consumption is paralleled in Canada. So there would probably be 2 to 3 million tons, or a total of 23 million tons, in the two countries. Of these 23 million tons only about 5% to 10% are in the category of reinforced plastics and the remaining 90% to 95% are either unfilled or plastics that contain bulk fillers to extend the resin. One can see that the filler market is therefore substantially larger than the reinforcement market. Also, some materials function both as a filler and a reinforcement and are often called reinforcing fillers, all of which can be very confusing.

Attention here is directed only to the 5%, or 3 million tons a year, that are reinforced. This is the market in which mica will play a part. Also, this is a rather substantial market in its own. Fiberglass, either rovings, mat, strand, fiber or flake, provides the greatest share of the reinforcement filler market where important properties are needed; properties that would make the reinforced resin a competitor with metal, wood or other high priced products. This reinforced market has been growing at a rate of 5% to 10% a year, with the exception of the 1979-1980 period, and it has a potential into the 90's that will become increasingly significant as mineral raw materials become scarce and the energy to recover or transform them grow in quantity and cost. In the 1977-1980 period, the dollar value of fillers used for reinforced plastics was on the order of magnitude of $500 to $600 million per year. Eighty percent of this was glass fiber and flake. Of the remaining 20%, calcium carbonate was in a range of $20 million, kaolin $10 to $12 million, silicas of all forms about the same $12 million, talc about $4 million and all other materials about $20 to $30 million. It is believed that mica will replace talc and calcium carbonate where product improvement of a special type, namely flex strength, stiffness, and heat distortion temperature are more important than impact, and also where compounders and molders are willing to pay a modest increase to provide this property. It will also substitute for certain glass fiber and flake materials in two instances; one where these properties are desireable and cannot be obtained from glass fiber and flake at a sufficient technical level and, secondly, where compromise can be made on other properties and cost is a factor. Bearing in mind that talc and calcium carbonate sell in the range of 5¢ per pound, untreated mica in a range of 10¢ to 15¢ per pound, treated mica in a range of 20¢ to 30¢ per pound and glass fibers and flake in a range from 80¢ to $1.10 per pound.

The technology of the 80's and 90's will be one of increasingly sophisticated engineering. The past century of overdesign, where materials were exceedingly cheap and demands on them generally modest, will change as materials become scarce, expensive, energy and labor intensive and the cost of labor and energy rise.

VI. ECONOMIC CONSIDERATIONS FOR THE INDUSTRY AND NATION

As we discussed earlier, mica in reinforced plastic and substitute or supplement asbestos products is priced between very low cost fillers and higher valued reinforcements. They thus bear the onus of proving merit compared to cheaper materials, proving cost reduction when compared to the higher priced materials. It has been our development premise that in all cases, it is useful to show the technical merit. Our marketing strategy, therefore, involves competition based on technical excellence preferred to competition on cost. The concept is more suited to the fabric of a technical organization such as Martin Marietta. Mineral and organic fillers can be produced from the very cheap materials and frequently are.

As compared to glass as a reinforcement, it is important to realize that fiberglass and glass flake are relatively new materials with an age of perhaps 20 or 30 years. For example, it was long believed that nothing would ever replace plywood or planks in boat construction. Not only has fiberglass effectively replaced these materials, but the glass industry has been so successful as to have this material called "Fiberglas". You don't buy a "plastic" boat, you buy a "fiberglas" boat. Asbestos, of course, is a legendary material and, with prices from $200 to $500 a ton, is very susceptible to replacement with a cheaper material. The problem is, of course, that nothing can truly replace asbestos in certain applications.

An economic consideration that's deemed important is the cost of obtaining suitable micas as fillers. The first consideration is the percent contamination or recovery and, although mica can be found anywhere in the world, there are few locations where it is particularly so since it is an industrial mineral selling at modest prices. Concentrations of mica occur in disparate areas, but primarily in large sections of western North Carolina in the U.S. This mica is muscovite of fine particle size. In the Malagasy Republic and in India, these latter are the large crystal sheets of mica that have been so valuable in the electronic industry. If mica occurs in deposits of below 50%, the separation and economics make it generally unattractive.

We believe that mica has a strong economic future in the coming age of raw material shortages and rapidly increasing energy costs. These both affect the plastics industry since rare and heavy metals will be replaced by plastics of lighter weight designed for specific end use. Plastics themselves, however, are produced from energy intensive fuels that will rapidly grow in price. Mica is a low energy intensive, low cost substance and provides a dual advantage of low weight, low cost and low energy consumption.

In conclusion then, let's say that mica, an ancient material not given proper respect, has finally, we believe, come of age and will become an important mineral, more noble than a filler and selectively valuable as a reinforcement, but certainly meeting the best characteristics of such in use.

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ASBESTOS AS A FILLER

M. COSSETTE

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ASBESTOS AS A FILLER

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ASBESTOS AS A FILLER

Abstract

The grades of asbestos used as fillers are described. The use of asbestos fillers in plastics to adjust the rheometry of compounds, and to improve mechanical and insulation properties, while reducing raw material costs, is described. Their use in various compounds with organic binders of all types is mentioned. The importance of the degree of fiberization, and of the absorption properties is explaines.

Biographical notes

Marcel Cossette graduated in Chemical engineering from McGill University. He began his career in the R.&D. Department ofAsbestos Corporation Ltd. He is presently Director of the QAMA (Quebec Asbestos Mining Association) Laboratory at the Université de Sherbrooke.

MC/mjb
12/11/81

ASBESTOS AS A FILLER

What is asbestos

The asbestos mined in Canada is of the "chrysotile" variety. It is a fibrous form of the mineral serpentine. Serpentine is a hydrated magnesium silicate, that also occurs as rock, like most other minerals.
Chrysotile is usually what people mean when they say asbestos. Other types make up perhaps 5 percent of world production, which exceeds 5 Mt/a. Chrysotile has the chemical formula $3MgO \cdot 2SiO_2 2H_2O$.

When chrystals of chrysotile are metamorphosed from the host serpentine rock, each silicon atom is in the center of a SiO_4 tetrahedral pyramid that co-ordinates with an octa hedral magnesium group.
This is shown in Fig. 1. As the crystal growns it forms sheets containing one layer of silica, and one of magnesia. Since the magnesia has a greater encumberment the crystal sheets curve as shown in Fig. 2. As the sheets grow, they curl into scrolls a shown in Fig. 3 that is an end view of two fibres. The inner diameters are about 50Å and the outer diameters are in the order of 250Å. Fibres generally have between 12 and 20 layers. The central hole, as well as the interstices between the fibres, may be empty, or partially, or completely filled with material of the same composition, either amorphous or chrystalline.

Fibres are separated from host rock by crushing in several successive steps, and aspirating the fibres released at each step. The fibres are dry sifted on rotating trommel screens to separate them into different length fractions, each of which may be fiberised to various extents to produce desired grades the final steps of

crushing and sifting yield the shortest grades for use as fillers. Another asbestos filler grade is composed of the dust collected in the dust control system of the mill and these products are termed floats.
Asbestos fillers may contain as much as 90 percent finer than 200 mesh; measured by wet sieving.

Fundamental advantages of asbestos

Fillers of all types are used in products as a diluent to reduce costs, or as a processing aid,
or to improve properties.
On a cost basis, at between 120 and 200 $/T, asbestos fillers could not compete against lower cost materials such as ground limestone. However, asbestos can be used as a processing aid by providing green strength in wet solids prior to setting; or rheological control to yield an appropriate consistency; or sedimentation control to support emulsions and suspensions.

However, the principal purpose of adding asbestos fillers is to confer superior properties on a products, such as:

- Stability to heat, moisture, and microorganisms.
- Insulation against noise, heat, and electricity.
- Resistance to wear, and to deformation under load or impact.
- Improved smoothness, hardness, and opacity.
- Resistance to chemical attack, leaching, and decay.

Most fillers are available in a range of particle sizes. However, asbestos can be obtained in the appropriate length distribution, and degree of fiberization. Furthermore various compounding processes will further increase the degree of fiberization, and these may be continued until the exact product consistency is obtained. The viscosity of a product can often be a function of the fibre length distribution while the degree of fiberization will influence the demand for the binder phase in use.

Asbestos fillers have the advantage of being fibrous materials, that offer the advantages of cellulose products without the moisture instability and putrescibility of the latter. Asbestos fillers offer the stability of minerals such as limestone, in addition to their controlled aspect ratios.

Range of products

The ranges of products containing asbestos fillers may be characterized by the binders they contain. Binders may be inorganic, resinous, elastomeric, bituminous, filmogen, or chemical.

Examples of inorganic binders where asbestos fillers can provide green strength include:

Portland cement; (1) in gunnite sprayed on tunnel walls to prevent erosion;
(2) in stuccos and plasters.
Clay binders (to maintain shape before firing).
Sodium silicate (to give dimensionnal stability).

Examples of resinous binders where asbestos fillers are process aids, and improve product properties include:

Thermoplastics; (1) to control squish, and flashing in injection molding,
(2) to improve stiffness, fatigue resistance, thermal stability and wear resistance.
Thermosets; (1) to reduce flashing, increase heat insulation and resistance to heat.

Examples of elastomeric binders where asbestos fillers confer resistance to heat, and improve the electrical behavior include:

Silicones; (1) stable for years at 200°C and take temperature peaks of 250°C,
(2) maintain elasticity at -80°C,
(3) readily sawed, bored, and milled.
Styrene butadiene Latex; high temperature strength, moisture resistance, and dimensional stability.

Bituminous binders where asbestos fillers act as thixotropes and provide resistance to deformation include:

Caulking and sealing compounds; viscosity control
Asphalt pavement; prevention of propagation of micro-fissures.
Roofing paper; provides dimensional stability against humidity.

Filmogen (film forming) binders, where asbestos provides resistance to wear, and to ultraviolet degredation due to its opacity include:

Linseed oil paints.
Alkyd resin paints.
Automobile rustproofing.

Chemical binders where asbestos fillers provide strength, and aid processing, include:

Silicate binders to graft silicones onto the chrysotile.
Phenolic binders to react chemically with chrysotile.
Ammonium phosphate to cross-link fibers.

Significant properties of the asbestos filler

The length distribution of the fibers is important in rheological applications. Even very short fibres (-200 Mesh = 34μ) can have very high length-to-diameter aspect ratios. The length distribution must be determined by wet classification by washing on a sieve because dry classification is influenced by the degree of fiberization. The length may be evaluated indirectly by measuring the viscosity or penetration resistance of a mixture in liquid asphalt. The longer the fibre is, the more strength, dimensional stability, and viscosity it will impart.

The degree of fiberization may be evaluated by air permeability that gives a measure fo the external surface of asbestos fibre bundles. Gas adsorption methods are not applicable because they also measure inner surfaces. The degree of fiberization may be increased by violent processing. Fiberization influences binder demand directly, and determines the consitency of a product.

Cleanliness is important. Naturally occurring associated minerals include non fibrous serpentine (antigorite and lizardite), and magnetite. These materials make no useful contribution, and may scratch the molds and the processing equipment. Cleanliness may be evaluated by suspending the asbestos filler in water, and allowing the rocky particles to sediment. Decantation will then allow the fibres to be separated from the associated minerals. Determinations of kerosene absorption will also give an indication of cleanliness because the rock fines absorb much less kerosene than the fibre fines.

Some product applications

To give an idea of various applications for asbestos fillers, the following non exhaustive alphabetical list of products is presented:

- adhesives
- asphalt roofing compounds
- asphalt pavement
- brake linings (molded)
- caulking and sealing compounds
- drilling muds and fluids
- flooring compositions
- floor tiles
- friction materials in general
- grease (fibre filled)
- hot and cold moulded products
- joint cement
- paint filler
- paper filler
- pipe wrap
- stucco grouting and concrete compounds
- thermoplastic mouldings
- thermosetting compounds
- undercoatings and sounds deadeners
- welding rod coatings
- waterproofing and dampproofing compounds.

If out of this list we pick one product; for example paper filler, here are some of the ways the asbestos filler can make a contribution:

- Opacity
- Ink printability
- Ultraviolet resistance
- Folding fatigue resistance
- Aging (Neutralises the acid formed by cellulose degradation)

Decreases porosity
Improves retention of whiteners.

To take another example: molded linings, the contributions made by the asbestos in this case include:

Reinforcement, and empartment of toughness
Wear resistance
Resistance to thermal degradation
Dimensional stability at high temperature
Compatibility with the other components.

A word about health hazards

During the last few years, asbestos has become the whipping boy of our news media who have generated an unwarranted panic. The truth is that the most elementary precautions allow us to use asbestos in complete safety. Contrary to what has been alleged in the media, the human body can tolerate significant dosages of asbestos. Since time immemorial the background level of asbestos in the atmosphere has remained unchanged. Accordingly, common sense work methods allow us to use asbestos with no more hazard than those presented by gasoline, and thereby allow us to take advantage of a mineral of unparalleled properties.

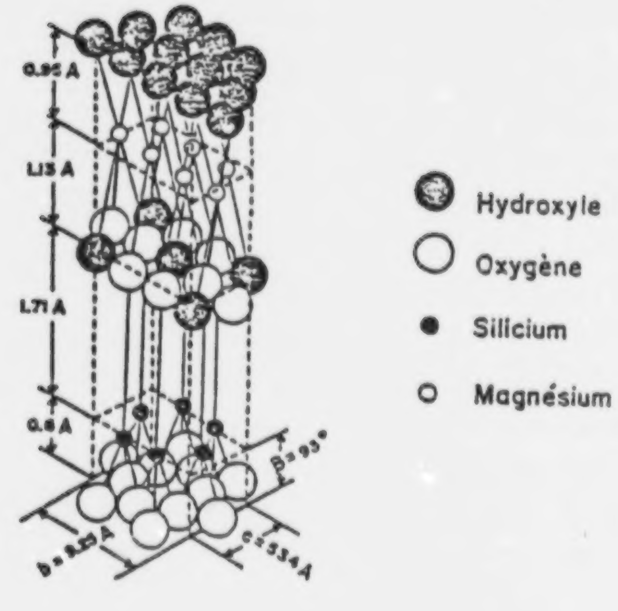
0.96 A
1.13 A
1.71 A
0.6 A
β = 93°
b = 9.23 A
c = 5.34 A
Hydroxyle
Oxygène
Silicium
Magnésium

Fig. 1 Unit cell in the crystalline structure of chrysotile (after Cossette, Lemonde and Massey. L'Union Médicale Can 100 759 (1971)).

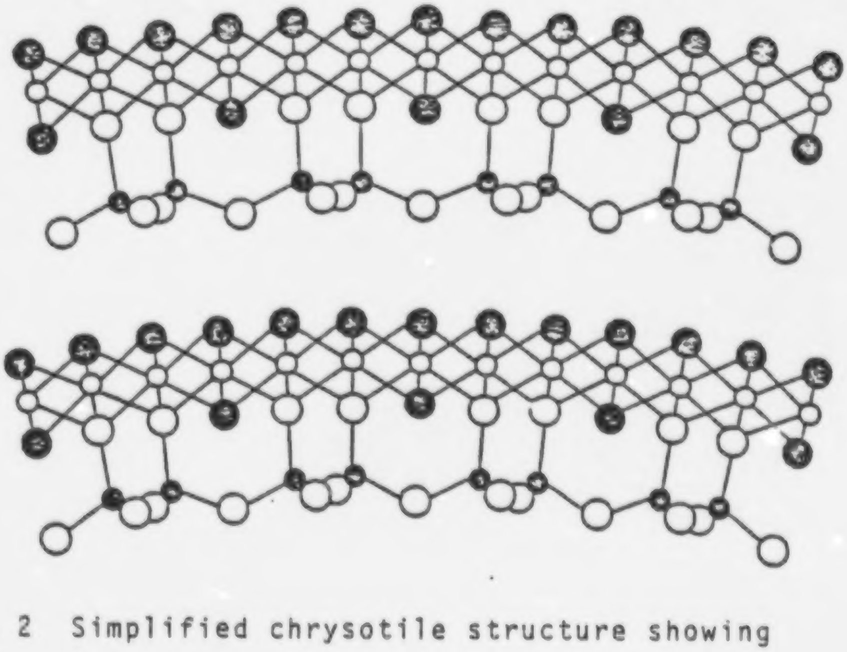

Fig. 2 Simplified chrysotile structure showing the curvature fo crystal planes (after E. Martinez. Can. Inst. Mining &Metallurgy Trans. Vol. LXIX, p. 414-20 1966).

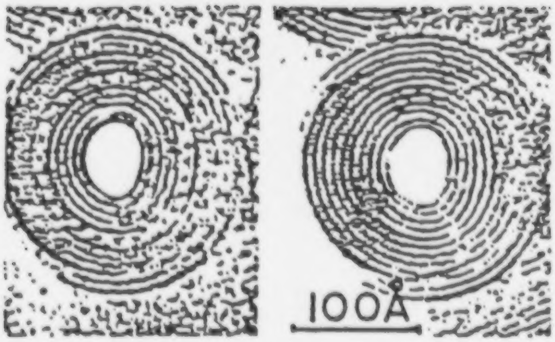

Fig. 3 End view of chrysotile fibers after K. Yada (in Acta Crystallographica, Vol 23 Part 5 p. 704-7, Nov. 1967).

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NEPHELINE SYENITE AS A FILLER IN PAINTS & PLASTICS

K.F. WEITZ

INDUSMIN LIMITED
DON MILLS, ONTARIO

NEPHELINE SYENITE AS A FILLER IN PAINTS & PLASTICS

K. F. Weitz, Indusmin Limited

NEPHELINE SYENITE

One of the most remarkable of the industrial minerals produced by Indusmin is nepheline syenite which is mined commercially in only three countries in the world - Canada, Norway and Russia. Indusmin's 2200 acre ore body and modern processing plant is situated at Nephton, 35 miles north of Peterborough, Ontario, Canada.

The nepheline syenite in this ore body is a unique combination of albite feldspar, microcline feldspar, feldspathoid nepheline and minor accessory iron-bearing minerals such as magnetite. It contains no free silica and resembles granite in texture and hardness.

More than one-half million tons of ore per year are crushed in several stages to sand products, which are passed over magnetic separators to remove the iron-bearing minerals. The resultant sand product is shipped as is, or ground in pebble mills to flour consistencies, depending on the market requirements. An extensive quality control program from mining control, for chemical uniformity, to sophisticated screening and classification equipment, to control particle size uniformity, assures consistency from one shipment to the next.

Because of this uniformity, nepheline syenite is a highly desirable raw material for the manufacture of glass containers used in industries such as brewing, soft drinks, food, cosmetics and pharmaceuticals; fiberglass insulation; ceramic whiteware products such as bathroom fixtures, floor and wall tile, china, artware and pottery. Nepheline syenite also has important uses as a paint extender pigment and plastics filler.

Although millions of tons of nepheline syenite have been mined, ore reserves have been proven that will meet increased market demand well into the 21st century.

Specific Uses in Paints and Plastics

Chemically, nepheline syenite is a sodium potassium aluminum silicate. As a paint extender, nepheline syenite offers an extremely high dry brightness (high 90's), excellent ease of wetting and rapid dispersion as well as high bulking value and low vehicle demand. In paint, nepheline syenite offers excellent exterior durability with outstanding tint retention and resistance to chalking properties.

With a Mohs' hardness of 5½ - 6, nepheline syenite is classified as an extender of medium hardness contributing significantly to the scrubbability and washability of interior wall paints. In addition, nepheline syenite's hardness permits it to act as a grinding aid in the dispersion of other pigments.

In aqueous solution, nepheline syenite exerts a pH of 9.9 thus contributing to the long term storage stability of latex paints; nepheline syenite also contributes significantly to the sheen uniformity of interior flat paints.

Nepheline syenite is a safe extender; it is non-toxic, low dusting and does not contain any free silica or quartz. In addition it is low in heavy metal content.

In plastics, nepheline syenite behaves as a low tint strength translucent extender particularly useful in the formulation of saturated deeptone colors at reasonable cost. Since the refractive indices of polyvinyl chloride plastic and nepheline syenite are identical (1.53), low loadings of filler (20 phr) are permissible without sacrificing the translucency.

October 19, 1981

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MINERAL WASTES AS POTENTIAL MINERAL FILLERS

R.K. COLLINGS

CANMET
OTTAWA, ONTARIO

Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

CANMET
Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

MINERAL WASTES AS POTENTIAL MINERAL FILLERS

R.K. Collings
Mineral Processing Laboratory

October, 1981

(For presentation at a CANMET - ORF Mineral Filler Symposium and for publication in the Symposium Proceedings, Toronto, Ontario, October 20-22, 1981.)

Project MRP-3.3.0.0.07
Primary Mineral Wastes

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT MRP/MSL 80-74 (OP&J)

MINERAL WASTES AS POTENTIAL MINERAL FILLERS

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ABSTRACT

A study was made of mineral filler usage by selected industries in two major areas in eastern Canada, each approximately 500 km (300 miles) in diameter with Toronto, Ontario, and Montreal, Quebec, as respective centres. Consumption of mineral fillers in these two areas probably totals 375 x 10^3 tonnes annually, or about 75% of the estimated Canadian total (500 x 10^3 tonnes), with possibly 50% of this amount being imported. Large accumulations of finely divided mineral wastes exist in these areas and although most are impure and distant from markets, some are favourably located and of interest as potential lower-grade mineral fillers in certain applications, e.g., asphalt and concrete mixes, in caulking and sealing compounds, in joint cements, and in some types of plastic. Filler requirements, and waste availability and characteristics, are reviewed and the possibility of utilizing specific wastes as fillers is discussed.

INTRODUCTION

The rate of generation of solid or semi-solid mineral wastes by Canada's mining, metallurgical, and chemical process industries currently is about 800 x 10^6 tonnes annually. Significant and increasing amounts of the coarser sizes of waste, e.g., waste rock and slags, are utilized for such purposes as railroad ballast and in road, dam, and breakwater construction, but use of the finer sizes, e.g., mill tailings, flue dusts, and chemical sludges, is limited. Possible applications for these finer sizes of wastes include use as mineral fillers in a wide variety of consumer products.

Mineral fillers are finely ground, generally inert mineral substances that are used in the manufacture of many products to reduce the consumption of more costly raw materials and to modify and perhaps improve physical properties. Although many minerals can be employed as fillers, those more commonly used include asbestos, barite, bentonite, calcium carbonate, clays, diatomite, feldspar, mica, nepheline syenite, pyrophyllite, silica, and talc. They are used either individually or in combination in the manufacture of a wide range of products, e.g., asphalt compounds, cleansers and detergents, concrete and concrete products, fertilizers, insecticides, linoleum and floor tile, paints and varnishes, paper, plastics, roofing products, and rubber.

Most mineral fillers must meet fairly rigid physical and chemical specifications, e.g., nepheline syenite in paint formulations and kaolin in paper, but other applications, e.g., asphalt mixes and concrete products, essentially require only that the filler be relatively fine, available in adequate quantities, and inexpensive. Mineral wastes from a number of mining, metallurgical, and chemical processing operations could satisfy these latter requirements. Whether or not a particular waste could be utilized would depend additionally on other factors, e.g., the location of the waste with respect to potential markets, the physico-chemical suitability of the waste as a filler in these markets (products), a selling price acceptable to both producer and potential consumer, and the demonstrated ability of the producer to supply consistently suitable material over an established contract period. Benefits that would be derived from the use of mineral wastes as fillers include lower costs, reduced imports of certain mineral fillers, conservation of mineral resources, and a limited beneficial effect on the environment.

This paper provides information on mineral fillers, examines a selected segment of the mineral filler industry of Canada, and identifies and describes a number of mineral wastes that conceivably could be used as alternate or supplemental sources of mineral filler material in particular products or applications.

Information for this paper was derived largely from CANMET Report MRP/MSL 80-65, "Mineral Waste Resources of Canada, Report No. 6 - Mineral Wastes as Potential Fillers"; May, 1980 (R.K. Collings).

USES AND CONSUMPTION OF MINERAL FILLERS

As previously noted, mineral fillers are used to reduce consumption of more costly materials in specific products. For example, calcined clays are being used increasingly to reduce the quantities of higher cost titanium dioxide pigment in many types of paint, nepheline syenite and calcium carbonate are used in plastics to reduce resin consumption, and fly ash and stone dusts are used in asphalt mixes to reduce bitumen requirements. Mineral fillers additionally serve to modify and improve physical properties, e.g., flow, colour, and tint retention of paints, and hardness, strength, and resistance to tear of rubber. Some products are heavily loaded with fillers. Bituminous compositions, for example, may contain 50% or more of filler by weight. Some, e.g., paint, paper and rubber, require high-purity, high-performance mineral fillers.

Fillers for paint, paper and rubber must meet rigid specifications with regard to purity, colour, particle size, degree of softness or hardness, etc. Other applications for fillers, such as their use in asphalt products, mortars and concrete, have less demanding specifications and therefore can utilize a wider variety of lower grade and consequently lower cost materials.

The most important filler minerals used in Canada, the applications or products in which they are commonly used, and estimated consumption are listed in Table 1. Although incomplete, these data indicate a consumption of about 500 x 10^3 tonnes of mineral fillers in 1977, if the 100 x 10^3 tonnes of fly ash used in portland cement concrete are included. Imports of mineral fillers are chiefly from the United States and are estimated at 250 x 10^3 tonnes per annum. Imports include part of the noted consumption of barite, bentonite, limestone, marble, mica, silica and talc, most of the diatomite, and all the fuller's earth and kaolin. Canadian production of fillers, by difference, would be in the order of 250 x 10^3 tonnes.

Mineral fillers vary widely in price or value, from $8 to $10 per tonne for lower grade fillers such as are used in asphalt mixes, to $100 to $125 per tonne for the finer grades of extender pigments used in paints, to $500 and more per tonne for speciality fillers such as the fumed and precipitated silicas used in rubber formulations. Assuming an average value of $50 per tonne, Canada's 1977 consumption of mineral fillers would be valued at $25 million.

Mineral wastes are of interest as alternate filler material in some lower grade applications. Such applications are not so dependent on high purity and whiteness of the filler but rather on other characteristics such as durability, particle size, density, etc. A good example in the use of waste limestone fines from aggregate preparation plants as filler in asphalt paving. Assuming that mineral wastes could be utilized in, say, 20% of the applications noted in Table 1, there could be a market for as much as 100 x 10^3 tonnes of mineral wastes as fillers in Canada. Mineral wastes normally would not command a high price, nevertheless even at $10 per tonne, the 100 x 10^3 tonnes of mineral waste believed to be of interest as mineral filler would be valued at $1 million. Although perhaps not a large figure as measured by today's standards, this does nonetheless represent the potential value of otherwise waste material. Also, the savings to consumers through use of such wastes conceivably could be several times this figure. Mineral wastes that could be considered in this regard are discussed more fully in the next section of this paper.

MINERAL WASTES OF INTEREST AS MINERAL FILLERS

Because of time constraints, the study of mineral wastes as potential fillers was restricted to two major areas in eastern Canada, each approximately 500 km (300 miles) in diameter with Toronto, Ontario, and Montreal, Quebec, as respective centres as shown in Fig. 1. Consumption of mineral fillers in these two areas probably amounts to 375 x 10^3 tonnes annually, or about 75% of the estimated Canadian total, with possibly 50% of this amount being imported. The remainder is produced locally. Large accumulations of finely divided mineral wastes exist in these areas and although most are impure and distant from markets, some are favourably located and of interest as potential lower-grade mineral fillers in, for example, asphalt and concrete mixes, in caulking and sealing compounds, in joint cements, and in some types of plastics. Thirteen typical waste types are listed and described in Table 2. These waste accumulations also are identified by numbers 1 to 13 and located on the map, Figure 1. The mineral filler applications for which they might be considered are noted in Tables 2 and 3.

A number of consumers of mineral fillers in the Toronto and Montreal areas have expressed interest in some of these wastes as possible replacement or partial replacement for higher cost mineral fillers that, in some instances, are being imported from the United States. Of particular interest are silica fume from silicon/ferrosilicon production at Beauharnois and Becancoeur, Quebec, silica dust from glass sand processing at Midland, Ontario, traprock fines from Havelock, Ontario, cement kiln dust and fly ash. Producers of these wastes in turn are keenly interested in marketing part or all of their output to reduce disposal costs. Research aimed at the use of these and other wastes in a number of consumer products is being carried out by several interested companies (see Tables 2 and 3, potential uses/applications).

Such interest is encouraging, unfortunately producers and potential consumers of mineral wastes often are unaware of each others requirements in this regard. A major effort must be made to bring about a greater awareness of the potential for utilizing mineral wastes. There is a distinct need for more published information on mineral wastes and possible uses on the one hand and potential markets and market specifications on the other. The need for information is basic. However, this is only the beginning. Following identification of a potential use for a particular waste a detailed, co-operative program of research and development is required to fully evaluate the technical and economic feasibility of utilizing this waste. If the program is successful, a mutually satisfactory price will have to be agreed upon by producer and potential consumer. The producer will want to adequately cover handling and processing costs whereas the consumer will want to establish a price significantly below that charged by current suppliers. He additionally will require some assurance of the ability of the producer to supply adequate quantities of specification-grade material over an agreed upon contract period.

THE CHALLENGE

Developing uses for mineral wastes, particularly in the complex mineral filler market, admittedly is not a simple task but the challenge is there for all willing to accept it and to work towards a fuller and more complete utilization of our mineral waste resources. There are as yet too few success stories, but developing interest by industry and government in conservation and recycling should produce a greater R & D effort in this area and could well result in a significantly greater utilization of these resources in the years ahead.

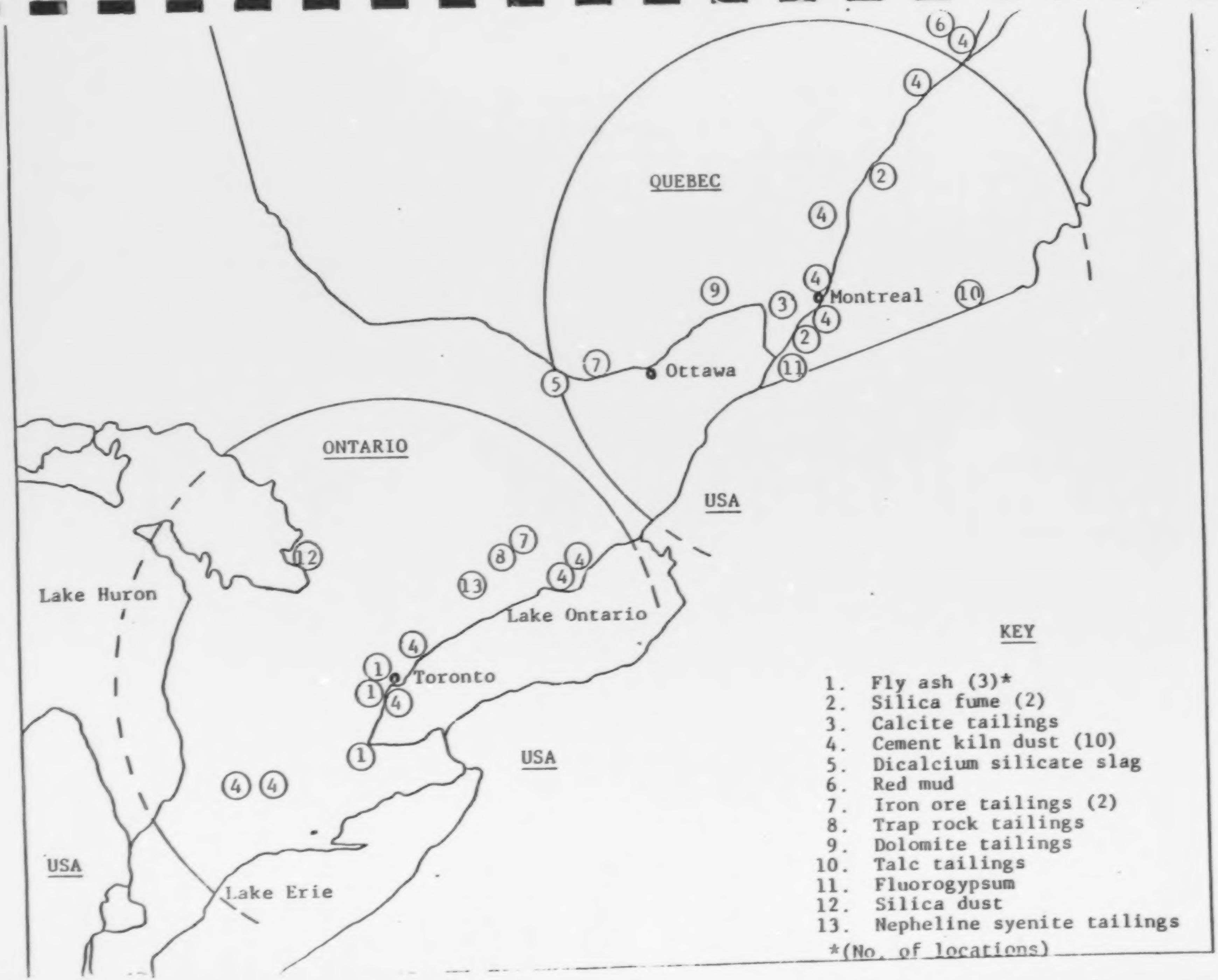
QUEBEC
Montreal
Ottawa
ONTARIO
USA
Lake Huron
Lake Ontario
Toronto
USA
Lake Erie
USA
KEY
1. Fly ash (3)*
2. Silica fume (2)
3. Calcite tailings
4. Cement kiln dust (10)
5. Dicalcium silicate slag
6. Red mud
7. Iron ore tailings (2)
8. Trap rock tailings
9. Dolomite tailings
10. Talc tailings
11. Fluorogypsum
12. Silica dust
13. Nepheline syenite tailings
*(No. of locations)
1
2
3
4
5
6
7
8
9
10
11
12
13

Table 1 - Consumption of selected minerals as fillers (Canada, 1977)(1)

Mineral	Consumption (tonnes x 10^3)	Product or application
asbestos	n.a.	floor tile, plastics, caulking and sealing compounds, asphalt products
barite	5.0	paint and varnish, rubber, plastics
bentonite	3.5	fertilizer, stock and poultry feed, rubber, paper
diatomite	16.0	rubber, paper, fertilizer and insecticide dusting
fuller's earth	6.0	soaps and detergents, paint and varnish, insecticides and pesticides
kaolin	150.0	paper, paint and varnish, rubber, tile and linoleum
limestone, marble	150.0	paper, paints, plastics, rubber, asphalt products, caulking and sealing compounds, fertilizers, insecticides
mica	4.0	joint cements, paint and varnish, plastics
nepheline syenite	6.0	paint, rubber, plastics
silica	20.0	gypsum products, fertilizers, paint and varnish, paper, roofing, rubber
talc, soapstone, pyrophyllite	34.0	paint, joint cements, gypsum products, roofing, pulp and paper products, rubber, plastics, insecticides, adhesives
fly ash	100.0	concrete products
portland cement	n.a.	asphalt mixes, roofing products
rock dusts	n.a.	asphalt mixes, mortars, concrete products

(1) Statistics Canada
n.a. not available

Table 2 - Mineral waste occurrences, current and potential uses, provinces of Quebec and Ontario(1)

Identification No.	waste	Location	Amount-tonnes (tpa or total)	Description	Uses	
					current (2)	potential (3)
1.	fly ash	Toronto, Mississauga, Hamilton, Ont.	750×10^3 (from 3 plants)	dark gray, mean diameter 10 µm but may range up to 150 µm, glassy, spherical particles, composed of compounds of silicon, aluminium, iron, calcium and carbon with minor magnesium, titanium, potassium, sulphur and alkali compounds.	road construction, land reclamation, additive to concrete.	asphalt mixes and in brick and block manufacture.
2.	silica fume	Beauharnois, Becancoeur, Que.	30×10^3 (from 3 plants)	gray, finely divided (85% minus 10 µm), principally consists of amorphous silica (SiO_2 varies from 85 to 99% depending on source), bulk density 0.25 g/cm^3.	high temperature insulation and in refractory cement mfg.	portland cement mfg. concrete and asbestos-cement products, in paint, plastics and rubber products.
3.	calcite tailings	Oka, Que.	4×10^6 (total)	gray, 50% minus 150 µm, principally calcite (75%), with silicates (18 to 20%), minor apatite.	soil neutralizer and fertilizer (limited use).	asphalt mixes, brick and concrete block mfg.
4a.	cement kiln dust	St. Constat, St. Basile, Joliette, St. Michael, Villeneuve, Que.	100×10^3 (from 5 plants)	gray-brown to white, minus 45 µm, principally calcium oxide (45 to 50%), with silicates (15 to 20%), and alkalies (5 to 20%); K_2O may range up to 40% in "by-pass" dust.	asphalt mixes	bitumen extender in asphalt mixes, as a coater for fertilizers and insecticides, soil additive, feed supplement for cattle, neutralizer for acid soils and effluents, in SO_2 abatement systems and in sewage treatment.

Table 2 - Mineral waste occurrences, current and potential uses, provinces of Quebec and Ontario(1)

Identification No.	waste	Location	Amount-tonnes (tpa or total)	Description	Uses current (2)	Uses potential (3)
4b.	cement kiln dust	Woodstock, Bath, Picton, Clarkson, Bowmanville, St. Mary's, Ont.	120×10^3 (from 6 plants)	gray-brown to white, minus 45 µm, principally calcium oxide (45 to 50%), with silicates (15 to 20%), and alkalies (5 to 20%); K_2O may range up to 40% in "by-pass" dust.	asphalt mixes	bitumen extender in asphalt mixes, as a coater for fertilizers and insecticides, soil additive, feed supplement for cattle, neutralizer for acid soils and effluents, in SO_2 abatement systems and in sewage treatment.
5.	dicalcium-silicate slag	Haleys Station, Ont.	40×10^3	gray, minus 2 mm, principally calcium orthosilicate, $CaSiO_4$, with minor magnesia, alumina and calcium fluoride.	none	in portland cement mfg., and in brick and block products.
6.	red mud	Arvida, Que.	1.5×10^6	brownish-red, minus 100 µm, consists principally of oxides of silicon, aluminum, iron, sodium and titanium.	none	filler/pigment in paints and plastics, brick and concrete products, fluorspar substitute in steel mfg., pelletizing agent for iron ore, recovery of contained minerals and metals.

Table 2 - Mineral waste occurrences, current and potential uses,

provinces of Quebec and Ontario(1)

Identification No.	waste	Location	Amount-tonnes (tpa or total)	Description	Uses	
					current (2)	potential (3)
7a.	iron ore tailings	Shawville, Que.	18×10^6 (total)	gray, 35% minus 150 µm, principally amphibole and quartz, with serpentine, talc, mica, feldspar.	none	bitumen extender and filler in asphalt mixes, brick and block mfg.
7b.	iron ore tailings	Marmora, Ont.	10×10^6 (total)	gray, 90% minus 250 µm, limestone, syenite, trap rock (40% SiO_2, 20% CaO, with alumina, magnesia), minor pyrite and pyrrhotite.	none	bitumen extender and filler in asphalt mixes, brick and block mfg.
8.	trap rock tailings	Havelock, Ont.	50×10^3	gray, 100% minus 850 µm, 35% minus 100 µm, trap rock, plagioclase, amphibole, quartz, chlorite (45% SiO_2, 22% Al_2O_3).	asphalt mixes	bitumen extender and filler in asphalt mixes, in brick and block mfg., in mineral wool manufacture.
9.	dolomite tailings	Kilmar, Que.	3×10^3	off-white, 100% minus 150 µm, principally dolomite magnesite and calcite, some serpentine.	none	bitumen extender and filler in asphalt mixes, in plastic pipe, in brick and block mfg.
10.	talc	Highwater, Que.	4×10^3	off-white, 85% minus 45 µm, principally dolomite and magnesite with as much as 20% of talc.	thermal insulation (experimental use).	in joint cements, in concrete paints, plastics and cleansers.

Table 2 - Mineral waste occurrences, current and potential uses, provinces of Quebec and Ontario(1)

Identification No.	waste	Location	Amount-tonnes (tpa or total)	Description	Uses current (2)	Uses potential (3)
11.	fluorogypsum	Valleyfield, Que.	30 x 10^3	gray-white, 75% minus 150 μm, principally fluorogypsum (75%) with anhydrite (25%) and minor quartz and fluorite, slightly acidic.	none	filler in plastics?, as set control agent in portland cement, in gypsum products mfg.
12.	silica dust	Midland, Ont.	variable, up to 300 t/week.	white, 85% minus 75 μm, principally quartz (99% SiO_2) with minor metallic (mill) iron.	autoclave concrete block mfg.	bitumen extender in asphalt mixes, brick and block mfg., in asbestos-cement products, in concrete paints.
13a.	nepheline syenite tailings	Peterborough area, Ont.	50 x 10^3 (from 2 plants)	gray-white, 50% minus 150 μm, principally nepheline syenite, with feldspar, mica, hornblende and magnetite (5%).	additive in portland cement	in asphalt and concrete mixes, for recovery of higher-grade nepheline syenite.
13b.	nepheline syenite dust	Peterborough area, Ont.	5 x 10^3	off-white, 60% minus 45 μm, principally nepheline syenite, plagioclase, K-feldspar and mica, with minor magnetite and calcite.	none	bitumen extender in asphalt mixes, in plastic pipe, joint cement, and brick and block mfg.

(1) Wastes with potential as mineral filler that essentially occur within 250 km (150 mile) radii of Montreal and Toronto.
(2) In Canada.
(3) Principally as filler but other uses also noted.

Table 3 - Selected potential applications for mineral wastes as fillers

Application	Mineral fillers typically used	Mineral waste substitute (1)
asbestos-cement products	calcium carbonate, mica, mineral wool.	calcite/dolomite tailings, cement kiln dust, silica fume.
asphalt products	calcium carbonate, talc, pyrophyllite, mica, asbestos, portland cement.	calcite/dolomite tailings, cement kiln dust, fly ash, rock dusts.
bricks, concrete, mortars	calcium carbonate, fly ash, diatomite, pumicite.	rock dusts and many types of mineral wastes.
caulking and sealing compounds	calcium carbonate, kaolin, talc, asbestos, silica.	calcite/dolomite tailings, cement kiln dust, fluorogypsum (?), fly ash, nepheline syenite, talc, silica fume.
drilling muds	bentonite, barite, mica perlite.	cement kiln dust (?), fly ash (?), chemical gypsum, talc.
fertilizers and soil conditioners	kaolin, diatomite, bentonite, perlite, vermiculite.	calcite/dolomite tailings, cement kiln dust, chemical gypsum, fly ash.
floor tile and linoleum	calcium carbonate, asbestos, talc, kaolin.	calcite/dolomite tailings, cement kiln dust, fly ash, nepheline syenite, talc.
insecticides and pesticides	fuller's earth, calcium carbonate, talc, pyrophyllite, bentonite, kaolin, diatomite.	calcite/dolomite tailings, cement kiln dust, chemical gypsum, talc, silica fume (?).
plastics	calcium carbonate, asbestos, mica, kaolin, barite, talc, pyrophyllite, nepheline syenite, diatomite, silica.	calcite/dolomite tailings, cement kiln dust, chemical gypsum, nepheline syenite, talc, silica fume.
rubber	calcium carbonate, kaolin, precipitated silica, talc, mica, barite.	silica fume.

(1) Some of these may, in fact, substitute for one or more of the principal minerals as well as filler minerals used in the manufacture of these products, e.g., cement kiln dust and silica fume to partially replace portland cement and silica in asbestos-cement products.

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CANADIAN WASTE EXCHANGE PROGRAM

R.G.W. LAUGHLIN

ONTARIO RESEARCH FOUNDATION
MISSISSAUGA, ONTARIO

CONCEPT

The concept of a waste exchange is predicated on the old adage that "one man's meat is another man's poison", or, as it might be restated today, "one man's garbage is another man's gold". Waste industrial materials may well prove to be a useful feedstock for another company.

In order that companies may consider using a waste material, they must first know of its existence. This is achieved by a Waste Materials Exchange which may be defined as a vehicle by which the availability of waste materials or by-products is made known to potential users. Other less formal definitions might be "industrial flea market" and "industrial bargain hunters' press".

BRIEF HISTORY OF THE ESTABLISHMENT OF THE CANADIAN WASTE MATERIALS EXCHANGE

In late 1976, Ontario Research undertook a study of existing waste materials exchanges throughout the world. As a result of the study, the establishment of a Canadian Waste Materials Exchange was recommended, to serve the whole of Canada. This approach is different to that being taken in the United States, where a number of regional exchanges have been set up. Canada is a large country geographically, but quite small in terms of population. We recognized that wastes are unlikely to transfer from Vancouver in the west to St. Johns, Newfoundland, in the east. Information, however, can readily travel across the country. Taking the regional approach only 3 or possibly 4 or 5 centres across the country would have sufficient industry to warrant the establishment of an Exchange. With a national exchange, all regions have access to the service, with very little additional cost. The costs of administration, publication and printing are minimized by this centralized approach. A national waste exchange also has the advantage of being able to establish a higher "profile" in terms of media and public interest.

While recommending the centralization of the mechanics of operating the Exchange, it was also recommended that the help of provincial and regional governments, industry associations, etc., be sought to promote local participation.

In October, 1977, Environment Canada contracted Ontario Research Foundation to operate the Canadian Waste Materials Exchange according to these recommendations for a two-year period, 1978 and 1979.

In late November, a brochure introducing the Exchange was mailed to 41,000 companies across Canada in the S.I.C. Manufacturing sector. This covered all manufacturers with 5 or more employees. We asked companies to indicate an interest in receiving our bi-monthly bulletin by returning a post-paid reply card. We also solicited wastes for inclusion in our first bulletin.

The first bulletin was mailed out in January, 1978. This was again mailed to the original 41,000 companies, plus to anyone who had indicated that they would like to receive it. It contained a total of 282 entries:

227 wastes available
27 wastes wanted
28 services available

The wastes are listed under 10 categories, as can be seen from the front cover of the bulletin shown as Table 1.

A typical page from a recent bulletin is included as Table 2 to show the listing format. All titles and instructions are in both official languages, French and English. Wastes are listed in whichever of the two languages they are submitted. This drastically reduces printing and mailing costs for the bulletins. Each entry has: a code number (e.g. A 006 is Available waste No. 006); and a regional identifier (e.g. Q), one of 23 geographic regions shown on a map on the bulletin's front cover. It then shows the quantity available and a brief description of the waste. In some cases, a more detailed geographic location is also identified.

PERFORMANCE OF THE CANADIAN WASTE MATERIALS EXCHANGE TO AUGUST 1, 1981

We have tried, on a continuing basis, to analyze the performance of the Canadian Waste Materials Exchange to determine the effectiveness of the programme. Table 3 summarizes the operation from January, 1978, to August 1, 1981. 4000 companies participate in the Waste Exchange programme. While we have never sought foreign participants, we have a number of U.S. companies using the CWME and even a few in Japan, India and the Philipines.

We have listed a total of 1,488 wastes. 89.6% of those wastes were of sufficient interest to generate at least one enquiry. The average number of enquiries per listing is almost 6. The number of waste transfers we have recorded is 215 or 14.5% of the listings on a numbers basis. Because we do not get involved in the negotiations between two companies considering an exchange, we have to rely on one of the companies letting us know that a transfer has occurred. This is not always done as rapidly as we would like. We continue to list wastes in successive bulletins until they transfer or the listers ask us to remove them from the lists. Thus, it is important that we know about transfers to keep our lists current.

The final two figures in Table 3 are, of necessity, approximations. We have attempted to estimate the annual tonnage of material transferred in those 215 recorded exchanges. Our best estimate is 185,000 tons. The "replacement" value of that 185,000 tons has been estimated at $4.85 million/year. This figure is computed by estimating the value of the raw material which the waste has replaced. Conservative estimates have been used throughout:

for example, for wood waste, the value of its energy equivalent at $1/million Btu has been assumed. This replacement value estimate can be readily criticized, and it should be used with extreme caution. It does, however, we believe, give us a reasonable estimate of an order of magnitude estimate of the economic impact of the Canadian Waste Materials Exchange.

In Table 4, data are presented by category. As can be readily seen from this table, the performance of the Exchange varies with different categories. We have been quite successful in encouraging transfers of organic chemicals, plastics and oils. We have been much less successful with acids and inorganic wastes.

The geographic breakdown of listings, enquiries and transfers shown in Table 5 pretty well reflects the distribution of industry across Canada. The enquiries and transfers are skewed in favour of Ontario, which may be explained by one of two reasons: either (a) the Exchange is located in Ontario, therefore it is easier for Ontario industry to participate; or (b) the concentration of industry in Ontario increases the opportunities for transfers.

In Table 6, the distances over which wastes transferred are summarized. While a large proportion travelled quite short distances, some travelled over 1,000 miles. This range of distances recorded for waste transfers further strengthens the original recommendation for a national Canada-wide exchange.

MINERAL FILLERS

Mineral fillers are generally listed under Category 5, Other Inorganic Chemicals. As can be readily seen from Table 4, this is the category which has resulted in the lowest proportion of transfers per waste listed at 6% compared with an average of 14.5%. This category includes both materials that could be regarded as mineral fillers, and smaller quantities of specialized inorganic chemicals such as potassium permangamate, copper sulphate, lead thiosulphite, etc.

Some materials which might be regarded as potential fillers are listed in the Miscellaneous Category, Category 10. This is a catchall for anything I cannot readily place in the other 9 categories. It includes everything from buttermilk to sponge toffee powder to 5000 tons per week of silica sand.

Within these two categories, materials which have been listed and which could be described as being potentially applicable as mineral fillers, include the following:

Coal Fly Ash and Bottom Ash
Oil Fly Ash and Bottom Ash
Silica Sand
Automobile Shredder Residue
Glass Cullet
Sand and Gravel
Granite Blocks
Glazed China
Cement Precipitator Dust
Diatomaceous Earth
Carbon Dust, High Ash
Crushed Fired Surface Clay
Sandstone
Gypsum
Phosphate Rock Dust
Dolomitic Magnesium Carbonate Silicate
Terra Alba
Blast Furnace Slag & Steel Slag
Fine Iron Ore Tailings
Nepheline Syenite

Of the exchanges or transfers we have recorded, the following are the only items which might be described as having potential as mineral fillers:

Anthracite Coal Dust
High Aluminum Content Dust
Coke Dust
Coke Fines
Biotite Stone
Sandstone
Glass Cullet
Asphalt Dolomite Mix
Used Firebrick

It is probable that the interest in these materials was for some of the components such as aluminum or carbon content rather than as filler. We have, therefore, to date been rather unsuccessful at finding users for waste materials to be used as fillers. I think, however, that this is partially explained by the fact that this is an area being actively researched, as evidenced by this seminar. As new uses for wastes as fillers are established, the Waste Exchange will plan an active role in matching generators with users.

COMPARING THE U.S. AND CANADIAN APPROACHES

In contrast to the single national exchange programme in Canada, the United States EPA has encouraged the growth of localized regional waste exchanges. There are advantages and disadvantages to both approaches.

The regional approach is in aggregate more expensive to operate because of the duplication of administrative centres. It does not result in as high a profile as would be enjoyed by a national exchange. It may also miss some transfer opportunities because of its limited geographic region. For example, some of our 1,000 mile plus transfers may not have occurred with a regional approach. The biggest advantage is the accessibility of the exchange when it is serving a limited area. Also, the exchange operator can have a much more comprehensive knowledge of the industry within its region than is possible with a nationwide exchange.

I do not believe that there is a "right" and a "wrong" approach to waste exchange operation. With the much larger industry base in the U.S., the regional approach is, perhaps, more logical. I think that the national approach and, perhaps more particularly, Environment Canada's funding of the exchange, allowed the CWME to become rapidly established and to make a fairly significant impact in Canada.

SUCCESS, FAILURES AND FUTURE PLANS

When the Canadian Waste Materials Exchange programme was launched, we had hoped to attract 4-5,000 participants listing about 4-500 wastes a year and achieve a 15-20% transfer rate for those waste listings. As discussed previously, we have come close to achieving all of these goals. Ontario Research has established a national exchange which enjoys industrial recognition across the country. Environment Canada have received praise for their continued sponsorship of the programme from both industry and environmentalist groups.

On the negative side, we had intended to try to make the project self-financing from 1980 onwards. This has not been achieved to date. We generated about 40% of our required operating budgets for 1980 and 1981. The remainder of our operating funds are being provided by Environment Canada, and the environment ministries in some of our provinces. Ontario, Nova Scotia, Quebec and British Columbia have committed funds, and the other provinces are considering support for the programme. This funding mix is rather appropriate; both levels of government and industry share a responsibility to develop solutions to the industrial waste disposal problem.

We have been less successful than we had hoped at finding uses for some of the problem wastes like contaminated acids, or dilute alkalis. The way in which we operate the Exchange with a bi-monthly bulletin makes it difficult for us to help industries with an immediate pressing disposal problem. Negotiation of a successful transfer often takes many months before both parties are satisfied with terms and safeguards as to quantity and quality of the waste.

Attempts have been made to expand operations by making appropriate links with U.S. exchanges. In May, 1980, all bulletins going to participants in British Columbia included a copy of the Oregon/Washington State bulletin. Geographically, north-south transfers make more sense than east-west in the Pacific North-west. In October, 1981, we are including listings from the NWX Exchange in Pennsylvania in all bulletins.

We would really like to expand these links with U.S. Exchanges. I believe that the utilization of waste materials is a global problem, which can certainly benefit from at least a continent-wide approach.

I would also like to expand the editorial section to include articles on research and on novel uses for waste materials. Any suggestions or contributions would be most welcome.

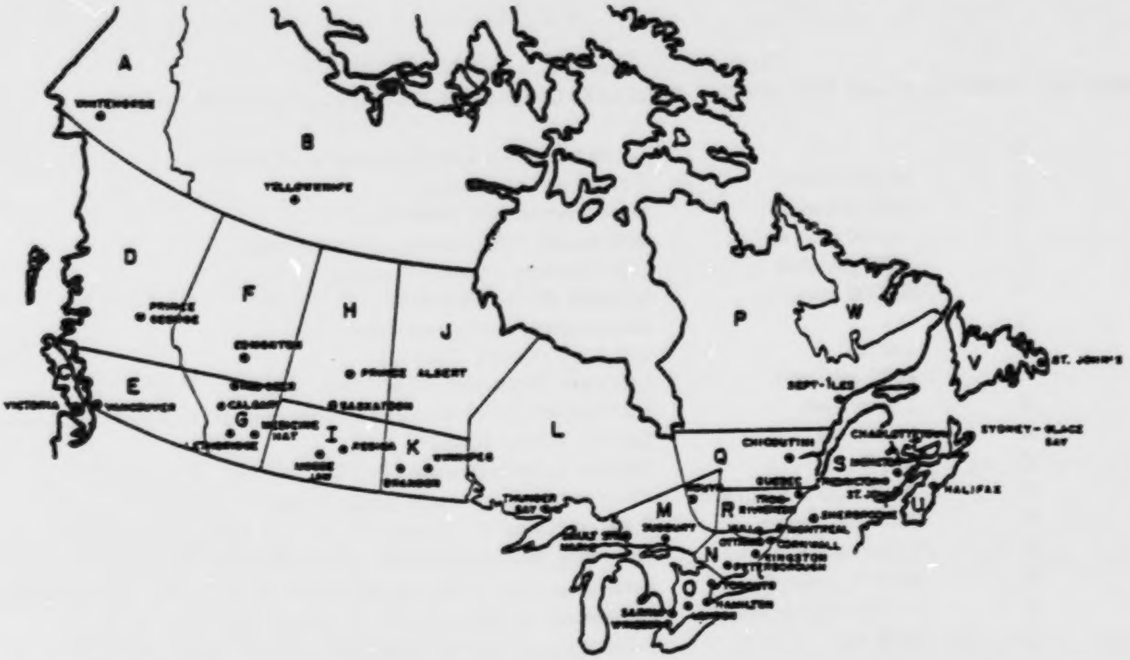
canadian waste materials exchange

TABLE 1

la bourse canadienne des déchets

BULLETIN NO. 22

JULY
JUILLET 1981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VANCOUVER
PRINCE GEORGE
PRINCE ALBERT
SASKATOON
MEDICINE HAT
THUNDER BAY
CHICOUTIMI
SEPT-ÎLES
ST. JOHN'S
SYDNEY - GLACE BAY
HALIFAX
QUEBEC
SHERBROOKE
MONTREAL
CORNWALL
KINGSTON
PETERBOROUGH
TORONTO
HAMILTON

The letters of this map are used to identify the geographic region in which waste materials are available or wanted. The letter appears as the last letter in the waste code number.

Wastes are listed in the bulletin under 10 categories:

1. Organic Chemicals and Solvents
2. Oils, Fats and Waxes
3. Acids
4. Alkalis
5. Other Inorganic Chemicals
6. Metals and Metal Containing Sludges
7. Plastics
8. Textiles, Leather and Rubber
9. Wood and Paper Products
10. Miscellaneous

Listings will appear in the language submitted.

Les lettres inscrites sur cette carte indiquent la région géographique dans laquelle des déchets sont disponibles ou demandés. Cette lettre apparait comme dernier caractère du code de déchet.

Les déchets sont inscrits au bulletin sous l'une ou l'autre des 10 catégories suivantes:

1. Produits chimiques organiques et solvants
2. Huiles, graisses et cires
3. Acides
4. Alcalis
5. Autres produits chimiques inorganiques
6. Métaux et boues contenant des métaux
7. Plastiques
8. Textiles, cuir et caoutchouc
9. Produits du papier et du bois
10. Divers

Les inscriptions paraîtront dans la langue de leur soumission.

ONTARIORESEARCH Sheridan Park Research Community, Mississauga, Ontario, Canada. L5K 1B3 (416) 822-4111

TABLE 2

WASTES AVAILABLE : DECHETS DISPONIBLES

Use Form 3 to enquire about these wastes if you think you could use them.

Veuillez utiliser la formule 3 pour obtenir des renseignements sur les déchets que vous pourriez utiliser.

1. ORGANIC CHEMICALS AND SOLVENTS : PRODUITS CHIMIQUES ORGANIQUES ET SOLVANTS

	Region/Région	Quantity/Quantité	
A 006	O	...	Crude napthenic acid still bottoms (Toronto)
A 058	O	60 gal/month	Toluol with silicone paint
A 170	O	5000 lbs/week	Slush from solvent processing
A 201	O	12,000 gal/year	90% toluol; 10% phenolics (Scarborough)
A 221	O	2000 gal/week	Light solvents, sludge (Toronto)
A 298	R	80,000 gal/week	Molasses stillage (Montreal)
A 415	G	...	Mixed rubber cure accelerators
A 547	O	100 lbs	U.C.L.-77 silicone (Toronto)
A 594	R	2000 gals/mois	Latex usé (Drummondville)
A 627	N	2 tons/week	1,2 Diamino cyclohexane/Hexamethylene diamine mixture (Maitland)
A 689	O	11,000 lbs	Calcium acetate powder
A 690	O	500 lbs	Calcium formate powder
A 708	O	20-25,000 U.S.gal/week	Mixed pentanes/pentenes/isobutylenes
A 783	G	2000 gals/month	Fusel oil (Calgary)
A 852	N	4 drums/year	Thermally degraded polyalkylene oxide H.T. fluid
A 938	N	6250 Kg/month	Filter press cake containing 50% plasticizers & 50% carbon and filteraid
A 939	N	17,500 Kg/3 months	Distillation residue, phthalic anhydrides and higher acids
A 945	O	3000 lbs	Trichloroacetic acid contaminated with Fe + H_2O (Sarnia)
A 962	O	2000 lbs	High heat silicone resin (DC803-50X)
A 966	E	9000 gal/day	Aqueous organic acids (5% acetic 1% formic + trace proprionic)
A 991	O	1100 lbs	Oil of sassafras (Fort Erie)
A 992	O	10,000 lbs	Alkali strippable polyester floor finish resin (Fort Erie)
A 1012	N	4500 gals/year	60% Di-Z-Ethylhexyl phthalate 40% trichlorobenzene trace Dicyclo-diepoxy carboxylate
A 1033	O	∿710,000 lbs	Solid naphthalene + anthracene (Toronto)
A 1034	O	∿260,000 lbs	Solid naphthalene (Toronto)
A 1035	O	∿360,000 lbs	Naphthalene + bakelite resin (Toronto)
A 1036	O	∿2,000,000 lbs	Gummy naphthalene residue (Toronto)
A 1037	O	∿30,000 lbs	Carbolate resin residue (Toronto)
A 1043	O	50 gal/week	Spent acetone (Barrie)
A 1045	U	100 gals	Styrene solvent cement (Dartmouth)
A 1046	O	646 Kg	Benzyl chloride (Burlington)
A 1047	O	1800 Kg	Methoxypropylamine (Burlington)
A 1050	O	1600 lbs	Ethylene Di-chloride
A 1078	O	5000 quarts	Acrylic lacquer, asst. colours, 30¢ quart (Toronto)
A 1086	U	470 pints	Styrene solvent cement (Dartmouth)
A 1087	U	117 quarts	Styrene solvent cement (Dartmouth)
A 1095	R	1500 gal/week	65% Naphtha, 35% Toluol solvent blend
A 1112	O	6000 gals	Water based paint (low viscosity) (Mississauga)

→ Indicates the start of new listings in each category

→ Indique le début des nouvelles inscriptions pour chaque catégorie

TABLE 3

Summary to date of the Operation of the Canadian Waste Materials Exchange

Number of Participating Companies	4000
Number of Wastes Listed	1488
Number of Wastes Enquired About	1333 (89.6% of listings)
Number of Enquiries	8539 (5.7 per listing)
Number of Wastes Transferred	215 (14.5% of listings)
Annual Tonnage of Wastes Transferred	185,000 tons
Value of Wastes Transferred	$4.85 million/year

TABLE 4

Analysis of Enquiries and Transfer of Available and Wanted Wastes by Categories - January 1, 1978, to August 1, 1981

	Category	No. of Wastes (A)	No. of Wastes Enquired About (B)	No. of Enquiries (C)	Enquiries per Listing (C)/(A)	Transfers (D)	Transfers per Listing (D)/(A)
1.	Organic Chemicals and Solvents	139	118	750	5.4	40	0.29
2.	Oils, Fats and Waxes	86	81	558	6.5	19	0.22
3.	Acids	46	43	276	6.0	5	0.11
4.	Alkalis	59	58	349	6.0	6	0.10
5.	Other Inorganic Chemicals	142	114	555	3.9	9	0.06
6.	Metals and Metals Containing Sludges	200	180	1165	5.8	21	0.10
7.	Plastics	117	111	1099	9.4	21	0.18
8.	Textiles, Leather and Rubber	225	203	1223	5.4	27	0.12
9.	Wood and Paper Products	317	296	1899	6.0	43	0.13
10.	Miscellaneous	157	129	665	4.2	24	0.15
		1488	1333	8539	5.7	215	0.145

TABLE 5

Geographical Breakdown of Listings, Enquiries and Transfers
Bulletins 1 - 21

	Listings		Enquiries		Transfers	
		%		%		%
West	245	16.5	1,056	12.4	29	13.5
Ontario	785	52.7	5,065	59.3	130	60.5
Quebec	408	27.4	2,207	25.8	46	21.4
East	50	3.4	211	2.5	10	4.6
	1,488	100.0	8,539	100.0	215	100.0

TABLE 6

Analysis of Distance Travelled by Wastes Transferred

		% of Those Stating Distance
< 50 miles	79	48.2
50-100 miles	20	12.2
100-200 miles	23	14.0
200-500 miles	16	9.8
500-1000 miles	13	7.9
> 1000 miles	13	7.9
Did not state	51	-
	215	100

ONTARIO RESEARCH FOUNDATION

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SYMPOSIUM

FLY ASH

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FLY ASH

Introduction

The Canmet Report on mineral wastes as potential fillers refers to fly ash as being not truly an inert filler. Whether the fly ash is used merely to improve physical properties or whether it imparts other physical or chemical advantages, it perhaps is not important. In Ontario some 1.5 million tonnes of fly ash is produced annually and it is therefore important that this significant resource be included in this forum. In North America the production of coal ash has reached some 60 million tonnes with clear evidence that this quantity will increase in years to come since coal represents the most widely distributed fuel. Historically, utilities have maintained a posture that they produce energy not coal ash and while this must remain their principle objective, there is no question that subtle changes in the many steps of power production can have significant influences on the characteristics of the ash produced. Fortunately, this message is beginning to filter into the generating stations. To fully utilize this resource or for any other that matter, it is equally important for industries that have a potential use also move in their thinking. To clearly identify their specifications and to review their historical tolerances so that some departure from the classical standards can be accepted provided there is no significant loss in end quality.

This need for flexibility is best illustrated by an early professor of engineering who stated "a specification is the last resort of wise men, and the Bible for fools". Anyone working on utilization of industrial by-products would be justified in wondering sometimes whether there are more fools than wise men.

Production

Coals are ranked by the ASTM primarily on the percent volatile matter and calorific values. In order, coals include anthracite, bituminous, sub-bituminous, and lignite, the latter having the lower calorific values. In Ontario, Ontario Hydro uses imported bituminous coal for its electric power generating stations. Well over 1,000,000 tonnes of the coal ash produced occurs at three stations, Lambton near Sarnia, Nanticoke on the shore of Lake Erie and the Lakeview Generating Station in Mississauga.

By way of definition, coal ash covers the range of by-products produced by burning coal. Eighty percent of the production is fly ash consisting of fine grained spherical particles, usually ranging in diameter from 1 to 100 microns and in simple terms is a silt sized particle. The remaining 20% is bottom ash which differs from fly ash in the way it is collected and is different in size being similar to a graded sand and gravel. Utilization of the bottom ash from the Power Generating Stations is relatively straight forward. It is used as a construction aggregate fill and in certain applications, where it is sized to meet market requirements, can be used for pavement skid resistance, blasting grit or roofing granules. This paper will deal only with fly ash.

The term fly ash as used in North America is described elsewhere as P.F.A. (Pulverized Fuel Ash), in the United Kingdom and as pozzolanic mineral admixture in specifications. Although it has a direct relationship to coal, it represents the inorganic fraction, its origin being the rock and overburden materials either within the coal or included in the mining process. Coal used by Ontario Hydro is of the bituminous variety either from the United States or from Western Canada.

It is worthwhile reviewing for a moment the basic steps in the process since these represent the first step in quality control of the by-product.

U.S. coal is used at Lakeview, Lambton and a blend of U.S. and Western Canadian coal used at Nanticoke. Blending is not a chance occurrence since it is critical to the operation of the boilers; based on known calorific values the power produced is directly related to the tonnes per hour of coal put through the pulverizers.

To comply with these power requirements, Ontario Hydro built a multimillion dollar blending facility at Nanticoke in the late 1970's. The coal is reduced in size, typically 80% passing the 200 sieve by grinding in pulverizers. Since the ground particles are transported into the boiler by the primary air system, which also acts as a source of oxygen for combustion, there is a classification on size at this point. In the boiler it is burned in suspension instantaneously at a temperature in the range of 1500°C. Since this temperature is above the melting point of the most of the minerals present, they undergo chemical and physical changes which include the formation of glass spheres of silicates. The several burning controls include coal rate, levels of primary and secondary air, gas recirculation excess oxygen levels, in either side of the boiler, etc. Although the overall efficiency is a complicated art, the requirement of high efficiency of combustion provides indirectly further classification of the subsequent ash that will be produced. From the boiler there are preliminary separations of the coarser particles either to economizer hoppers or through mechanical precipitators depending on the design of the station. The majority of ash collected and in fact all of the ash that is considered for utilization, is recovered from a series of electrostatic precipitator rows. Typically three or more rows of precipitators intersect the flue gas stream and in effect individually sort the ash into separate collection hoppers. In some stations the accumulated collection is transferred to holding silos, in others individual rows are tapped. In this way, there is reasonable classification of the ash in terms of size and in terms of any carbon content that remains at the end of the heat retention cycle.

It is routinely assumed that by-products must inevitably be irregular and random in quality. It is true that there are differences, and differences that must be examined where the recovered ash has potential in several similar markets. It should be obvious that the controls built into the combustion cycle in themself provide tolerances to the characteristics of the by-products and obviously the method of collection has built-in classification.

At stations where effort is made to market the by-product, there would usually be additional quality tolerances imposed by blending, selection and in some cases additional classification for size. In the future, it could be expected that additional classification will emerge to separate components as to size, carbon and possibly into the individual minerals.

Properties

As discussed earlier, coals are ranked according to their calorific value. Reference to published analysis of fly ash from sources throughout the world show surprising little differences in chemical composition. Surprising in that fly ash is supposedly a by-product, often regarded as a waste, for which one would expect wide differences in composition. The main differences that occur seem to be between differences in coal source where the sub-bituminous and lignite coals produce ash with relatively high lime components, say 15 to 25% CaO, in contrast to the 3-6% level in bituminous coals. Differences also occur in the amount of unburned carbon that exist within ashes from different sources, low carbon ashes in the range of 1 to 4%, higher ashes with carbons ranging from 8 to 12%. These differences in carbon are the result of coal type but also occur due to variations in station operation, and in the quantity of inorganics in the coal source. Differences can occur because of maintenance of pulverizers, variations in excess oxygen in the boilers, variations in the balance of primary and secondary air, etc. Variations can also occur where station runs at a fairly steady output of power (base loaded) versus stations that are required to provide peak demands of power. These differences are in many cases exaggerated as to their effect and certainly there are opportunities to even out some of these differences by selection or classification.

The fly ash, as discussed earlier, is a silt sized particle typically one to 100 microns in size range and, without classification, will usually have 20 to 25% retained on a 325 sieve.

Petrographic analysis has shown that glass is the primary component of ash with finer particles generally containing a higher proportion of the glass constituent. Other components include magnetite, hematite, carbon, mullite and quartz. A unique characteristic of fly ash relates to its particle shape. The predominant oxides of silica, alumina and iron exist essentially as individual spheres, a characteristic that can be singularly important to a material filler. As an example; when fly ash is used in concrete, there is a distinct chemical effect as discussed later, but in the initial stages mechanical particle behaviour is important. In any mixing of fluid and particulates, energy is used to overcome inter-particle friction and the work required to overcome particle interlocking. Introduction of spheres reduces this latter component of work with the result that there are improved mixing characteristics, improved workability, etc.

Any residual carbon exists usually in the coarser size range with a cinder-like appearance; for certain applications, carbon can be a disadvantage because of its high absorptive potential. In others the potential for absorption or the expected fuel value of the residual carbon can be an advantage.

Unique Characteristics

The size range and the shape of the fly ash particle is one special feature and is, as discussed, the consequence of cooling of molten silicates (glass) in an air stream. This then differs from many other by-products that are derived from grinding or crushing/blending operations. Fly Ash, in summary, is a combination of oxides, the principle one being silica and depending on source or selection exists in combination with some fraction of carbon. In this connection there are opportunities for selection of higher carbon/silica combinations, for industrial applications that have need of carbon. Historically, lower carbon applications have been sought, aimed specifically at cement markets.

Perhaps the most popular and most frequently written utilization of fly ash is its use in cement products; these include concrete, block, concrete brick, pipe, mine backfill. In other words, most if not all areas where cement is traditionally used. The word pozzolan as used in current specifications develops from the town of Pozzuoli, Italy, where as long ago as 300 B.C. natural volcanic ash was used with lime to produce mortar. As a consequence of this historic use, a pozzolan in todays terminology refers to a material which in of itself has little cementitious value but which in the presence of lime combines to produce additional cementitious components. Fly ash from bituminous coal contains relatively small natural levels of lime. However, when used with cement, the fly ash will combine with the free lime that is produced by hydration of the cement to form additional permanent cementitious compounds.

Fly ash that is derived from sub-bituminous or lignite coals can contain a significant portion of lime to the extent that they in themselves possess hydraulic properties; not to the extent of commercially produced cements but perhaps more similar to ground hydraulic slags. The fundamental similarities of cement, fly ash and slags are perhaps surprising given the obvious disparity in their names. Less so when recognizing that all involve similar thermal processes, combinations of lime and silica albeit in different proportions and all produce hard durable calcium silicates of one type or another. Their differences result primarily from differences in sequence of combination and their relative proportions. Using this simplistic view of the fundamental steps in their evolution helps understand that the supplementary cementing materials do not derive their properties by accident. As discussed, the behaviour of fly ash and its value in combination with cement, or cement and slag is now well established.

There is another potential benefit that has been given little attention. This refers to the difference in energy demand for processes that involve heat and the burning or thermal treatment of silica. Materials that are amorphous rather than crystalline could be expected to require less heat to return them to their reactive temperatures. Alternatively, the temperature required for kiln reaction kinectics, as one example, may be lower than where the raw material is a naturally occuring source of silica. There is some evidence from limited comment in the cement industry transcripts, and by work in ceramics from the Bureau of Interior on waste glass that there are significant energy benefits to utilization of fly ash as a source of silica rather than traditional sources of clay, sand or shale; these energy benefits are quite separate and distinct from those energy benefits that would be calculated from the residual percentage of carbon that the fly ash may contain. Its use as a raw component of cement manufacture, as distinct from the classical use to produce "blended" cement (when fly ash and cement in combined after the kiln) represents a large potential for mass volume use where energy is a potential, not merely chemistry adjustment of the raw feed.

Uses (International and Canada)

Pozzolan:

Ready Mix Concrete

Fly ash pozzolan, under the Canadian Standard Association specification, can be used to replace a portion of the cement used in concrete. This use began in North America historically as a component of the cementitious content in large dam construction, primarily for improvement in workability and for reduction of the heat of hydration. In these applications with fairly low target strength and little emphasis on early strength development, it was typical to use a 1 to 1 replacement by weight. This concept while still used in some areas and for certain ashes is too simplistic for modern day commercial concrete which has to meet a range of customer needs including sufficient early strength development. Regrettably, this historic use has left the impression in many designers minds that the use of fly ash must always have a consequence of lower early strengths. Research at Ontario Hydro has developed procedures for design that permits equal early, mid or long term strength target dates. The basis of such design is to provide a combination of cement and pozzolan which at the required amount would provide the target strength and at the date required. The approach is straight forward and consitutes considerable economies to the concrete producer. Other advantages include workability due to the spherical shape, increased cementitious content (by mix design), improved density, lower permeability and for special requirements, lower heat of hydration and improved resistance to groundwater sulphates. With appropriate design, there are no disadvantages to the use of fly ash, only advantages and economy. This, in todays climate of energy management, is responsible for a growing use in commercial concrete.

"Disadvantages", or perhaps more correctly "differences" from historic technology include; concrete is darker in a plastic state and cures to a bluish grey, the fly ash must be handled in a separate pneumatic silo in much the same manner as cement and additional dosage of admixture can be a requirement where in air entrainment is specified. With over 3 million cubic metres placed in Southern Ontario during the past decade, the colour has clearly not been a consequence, the return on investment for a silo requires less than one year so that disadvantages as such are more imagined than real. For comparison; in several States south of the border, entire industries now utilize fly ash throughout their production whereas in Ontario the evolution is still in relatively early stages.

Block:

Fly ash pozzolan can be used as a cement replacement in low pressure block operations; with replacements of about 20% of the cement being reasonable. The colour, a principle concern to the producer, is again a bluish grey tone somewhat warmer than the conventional grey block but nevertheless a difference that has to be faced.

In autoclave operations, the block produced by replacement of the silica flour with fly ash has a colour almost identical to that presently produced using lightweight aggregate in the same autoclave process; the block has a light bluish tone, generally warmer and more uniform than the customary colour. Again there is economy, but given the recent switch to metric there are constraints on inventory. Imperial, metric, regular and lightweight block are now carried and since inventories should be depleted somewhat before a change to a slight colour variation could be handled with relative ease. Depending on silo capacity, fly ash can be added to amend cement and silica quantities, or to entirely replace the silica.

Concrete Pipe

Fly ash pozzolan can be used in either packerhead or vibration equipment as a replacement of cement to about 20-30%. It also can be used for provision of additional fines usually in non-reinforced pipe. Advantages are obviously economy but in terms of quality, additional fines improve the product against permeability criteria. Compression strengths or strengths measured by 3-edge bearings are not at risk.

Precast, Grouts, Concrete Brick

There is little experience in Ontario in precast work although there is sufficient evidence from the block experience to indicate that there is some potential. Given restrictive high early strength performance, aesthetics of colour, its use is probably more restricted.

Fly Ash has of course been a well established ingredient in grouts on an international basis and in"pre-pak"work offering the benefits of workability,improved pumping etc.

Fly Ash has been used to a limited scale in concrete brick operations in Ontario. The diversity of colours that are mandatory in this industry give some restriction to its potential.

Mine Backfill

One single market that is very significant to the use of fly ash, specific to Ontario, is in the area of mine backfilling, in technology that has developed with great strides to permit additional recovery of ore. This technology is now well established having a requirement for stabilizing waste tailings to relatively low strengths (30 to 50 PSI) for mass fill with additional strength provided for mine floors. This traditionally has been an area of high consumption of cement and obviously mining has looked to its own slags as being potential replacements at least in part of the cement consumed. Slag will no doubt have a role to play but it will require energy to convert it to a form that is useful. The potential use of fly ash is largely unexplored with prelimary tests approaching this technology on the basis of concrete. Given the low strengths that are required it would be more appropriate to study the geotechnical parameters that are important. Obviously, with the high fluid volumes that are involved, considerations of consolidation, time dependent strength, permeability, influence of pore pressures all lead to a fundamental approach involving effective stress considerations rather than the total stress analytical procedures that have been historically used.

Stabilization

From work at universities or through a variety of proprietory products there are several uses of fly ash that are now been established in selected geographic locations. Much of them evolve round the combination of lime and fly ash and the pozzolanic characteristic which has been described.

Stabilized Base

Under the proprietary name of Base-mix in the U.K., combinations of cement and fly ash have been used, combined by high speed mixer and used as the base or sub-base layer of pavements; either for highway or parking areas. In the United States, manufacturers have followed this procedure but utilize lime with fly ash and in some cases provide an aggregate component. Pioneer work by Barenberg (University of Illinois) and now through State specifications, or proprietory products, this technology utilizes fly ash to give high strength mixtures which allow reduction of conventional granular thicknesses. There are some technical differences between the use of cement and lime but the principal is essentially the same.

A similar approach involving a more fluid consistency, has been adopted by Dufferin Concrete in Southern Ontario with their product K-Krete. It is perhaps interesting that in North America,approaches like these tend to follow from efforts of individual entrepreneurs whereas in other countries (eg. Belgium) the production of "stabilized sand" is an industry in its own right. The essence of the Dufferin work is to utilize the blending features, intrinsic to a concrete plant, to combine low grade aggregates with fly ash and cement to produce a controlled density (cemented) fill for the construction industry. Preliminary work at St Lawrence Cement a number of years ago showed that kiln dust could be a useful component of the mix.

Waste Treatment

Fly ashes which contain a relatively high proportion of carbon offer a possible medium for adsorption of waste liquids. Work has been done in the United States to investigate the potential for treatment of water and for the treatment of sewage sludge with fly ash. In simple mechanical terms, the particular grain size and shape of fly ash allows a higher absorption of liquid than does a conventional fine grained sand. This is illustrated by the wide difference in water requirement to reach optimum compaction moisture; for sand an optimum level would be about 8 to 10% whereas for high carbon ashes it would typically be 25 to 30%. This is particularly a physical absorption and ignores for a moment the potential for adsorption by activated carbon that is present in significant quantities in some sources of fly ash. Liquid waste then can be physically altered to permit ease of handling and by further addition of lime or other additives can be solidified or fixed. Other versions of this treatment include the sequential treatment by acids and alkalis, typically waste products, to initially leach and then fix the heavy metal components of some wastes.

Fillers

It is perhaps ironic that the section of fly ash as an inert fillers would represent only a small proportion of this presentation.

Asphalt

There is little experience of using fly ash as a filler in asphalt products in Ontario; Ontario Hydro have manufactured fly ash/asphalt pavements for test sections which have proved durable to date. Essentially the role of the filler in this case has been to modify the aggregate structure to reduce the requirement for asphalt cement. In Southern Ontario, aggregates are generally close to ideal in gradation and where necessary contain significant portions of screenings; sufficient to reduce the cement requirement to optimum levels so the need for additional fine grained filler does not appear to be warranted. This is presently a review by the MTC for alternative mixtures that would provide advantages of skid resistance and resistance to polishing. In Southwestern Ontario through into Michigan many of the aggregates are washed and their open structure permits more readily the use of a fly ash filler. Work sponsored by Detroit Edison several years ago at the University of Michigan clearly demonstrated that fly ash has similar value to the classical Trinidad fillers. This use represents a significant tonnage in Michigan.

Plastics

Experience to date with the use of fly ash in plastics from parts of the United States or particularly in the U.K., have tended to concentrate on the cenospheres that are present in some lagoon ashes. These are spherical hollow inorganic particles light in weight, also referred to as floaters and which have an obvious application in the plastics industry as a means of reducing weight and reducing the requirement for resins. Whether the fly ash as normally produced will have a similar place remains to be seen.

Soil Modification

Subgrade

Work is in progress at the present time at the University of Western Ontario under Dr. R.M. Quigley reviewing the potential for treatment of subgrade soils with fly ash as an alternative or in combination with the classical approach of using lime. The basis of this technology is the reduction in plasticity to in effect modify the clay either to reduce its reaction under frost effects or to improve its strength so that subsequent pavements can be reduced in thickness. Results to date show that there are significant differences in the reactivity of fly ash with calcium or magnesium based lime additions.

Industrial processes

There is obviously a wide spectrum of industrial processes which variously use combinations of silica and coke as raw materials, either as the key ingredients or as amendments to the principal volumes. Continuing efforts to utilize fly ash have developed certain processes that are unique to the fly ash industry; these will be discussed first.

Lightweight Aggregate

The production of lightweight aggregate from expanded clay and shales has declined in recent years in North America as energy costs have risen. Processes developed by Lytag, a division of the Laing Group, U.K. and developed over the past 20 years to produce a high quality, lightweight aggregate. The essence of the process involves the pelletizing of fly ash,sintering on a travelling grate and utilizing the residual carbon as a source of fuel in the process. In the United Kingdom this process consumes a considerable annual quantity of fly ash (close to one million tonnes).

Gas-Concrete

From developments in Sweden and in the United Kingdom, gas-concrete blocks are produced under the trade names of Thermolite, (a division of Laing) and by Celcon. These processes involve combinations of fly ash, cement, sand, lime and aluminum powder formed into a slurry and cast. The evolution of gas causes the mixture to rise within about one hour to normal temperatures, sufficient to allow slicing of the resulting cake by a series of transverse and longitudinal wires to produce blocks. Subsequent steaming and autoclave is used to produce a lightweight block of densities of 20 to 40 lbs per sq. ft. and strengths of about 300 to 400 PSI. These are compatible with the historic methods of house construction in the U.K., and are somewhat lower than our historic strength values for concrete block. This process is a high use for fly ash but is somewhat specialized to countries abroad. Principle feature relates to the thermal insulation that is involved in such a lightweight product.

Mineral Wool

Experiments have been made with the use of fly ash as a source of silica for mineral wool production. This has been done at the University of West Virginia and also in small scale test at the University of Toronto. There are advantages reported in the reduction of cost of flux. Colour is reportedly a disadvantage, being light grey rather than the customary white.

Cement Production

Production in Ontario involves a variety of sources of silica. Clay, shale or sand from local or on-site quarries are used to modify raw feed to the cement kiln. It is in these areas and for specific plants where there appears to be a good potential for high volume use of fly ash. In principal, the fly ash would provide the required chemistry adjustment given the similar oxide distribution to conventional materials. The additonal advantages would relate to residual carbon and the differences in burnability of the silica form in fly ash.

Many steps have to be reviewed to determine whether this is a real potential. Clearly experience abroad, (U.K. and Europe) shows that fly ash is successfully used to modify limestone chemistry in both dry and "conditioned" form for both wet and dry processes. This use should not be confused with the specifications that deal with the production of blended cements where fly ash pozzolan is added after the kiln to produce a 1 P cement as it is known in the United States or a 10P which is currently in specification here in Canada.

Clay Brick

Work has been in progress now for about two years with the Brampton Brick Company, Ontario, with assistance from the Federal Government to utilize fly ash as a partial replacement for shale. This area of use will be discussed by Mr. Howard Penn in a subsequent paper at this conference. In essence, energy recovery, improvements of plasticity, additional product lines and conservation of existing resources are among the elements being studied.

Smelting

Preliminary look is being given to high carbon fly ash as a possible alternative source of silica and petroleum coke for Electric Furnace Smelting. The differences in flux behaviour, reduction of selected metals by carbon are areas of study.

Glass

Fly ash has been reviewed for use in the multi-component mix used in glass manufacture. Obviously the presence of iron restricts its use to certain colours. The fine grain characteristics of ash potentially appears a problem to the furnace atmosphere and the dust collection systems. It is for these types of technology that one questions whether some pretreatment of the ash either to remove iron or pelletize to assist in handling could be a benefit given there is reasonable evidence that the industry has an appropriate use.

Rubber

There has been preliminary work in the United States on the use of fly ash in rubber manufacture. Recognizing that conventional raw materials do include carbon and clay, only time would tell whether these equivalent components of fly ash can be put to useful purpose by the rubber industry. Investigators at the U.S. Bureau of Mines in Morgantown, West Virginia, of the Energy Research Centre have done experimental work on tire threads containing fly ash with indications of improved traction and skid resistance. Up to 2 lbs of ash could be added to each tire without effecting the conventional properties in an appreciable manner.

Summary and Conclusion

From the work we have done, we see the mass utilization of fly ash best coming from the areas of cement replacement, processes that require silica and energy reduction, conversion into lightweight aggregate and in the growing technology of waste treatment. The potential as an industrial filler is largely unknown to us. It is in a forum such as this that we would hope to effect a reaction from attending industries where fly ash may be of some direct value in their process or as a component to improve their by-products. We are constantly reviewing whether there is a need to classify fly ash into several components, either by size or constituent.

Historically, there has been a tendency to expect a by-product to be accepted despite its shortcomings. In some cases, this may be true. But to be truly a resource material, this is a philosophy that must be questioned. There are few resources that can be mined and turned to the marketplace without some cost component.

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SYMPOSIUM

STEELMAKING WASTES:
A SECONDARY RAW MATERIAL

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HAMILTON, ONTARIO

(49)

STEELMAKING WASTES:

A SECONDARY RAW MATERIAL

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Presented at

JOINT ORF/CANMET SYMPOSIUM ON MINERAL FILTERS

October 20, 1981

Steelmaking Wastes: A Secondary Raw Material

INTRODUCTION

Recycling is not a new innovation for the steel industry. Reusing by-products is more of a tradition than an exception. Specific surveys have shown that about 80% of by-product materials are either recycled internally or sold as secondary raw materials. The remainder are disposed of as landfill. Scrap iron, iron oxide scale and slags are some of the common materials with which most are familiar as candidates for recycle. However, my interest today is to make you aware of some other interesting materials which are reusable but which are not reused entirely. The challenge is to find more economical ways to reuse materials and reduce existing disposal problems.

Specifically, I have selected three types of dust and intend to discuss them on the basis of their source, characteristic and reuse potential. They are:

1. Steelmaking Lime Fines.
2. Acid Regeneration Plant Iron Oxide Dust.
3. Steelmaking Iron Oxide Dust

1. STEELMAKING LIME FINES

Raw materials such as lime, dolomite, iron ore pellets and flux additives are required in fairly large quantities in the production of steel. The materials are delivered to Stelco's plants at Hamilton and Nanticoke mainly by truck to special unloading stations. They are then automatically carried by conveyors to storage bins located in the Steelmaking Shop. Although the materials are screened before delivery to the plant, transportation and handling will form dust through abrasion. On account of the dusty nature of the material, an elaborate air cleaning system is required and it collects daily about 5 tons of dust at our Hilton Works plant in Hamilton. Lesser amounts are collected at Lake Erie Works.

The dust quantity is not particularly large but we were interested in minimizing a disposal problem and, therefore, looked at methods for reusing the dust. First chemical tests revealed that the dust is rich in unslaked lime and the composition was fairly constant. Because the dust comes from a common air cleaning system, it contains portions of elements found in the raw materials. As a result, two reuse options were explored, namely:

- charging the dust directly back to the steelmaking process and
- using it for treating industrial liquid wastes.

The first and preferred option did not work out. The dust was too fine in size and not sufficiently dense for it to be reused directly in steelmaking. The dust either floats or is sucked out of the furnace by the exhaust system.

A pelletizing or agglomerization step is required first and this means more equipment and capital costs could not be justified.

However, the dust proved to be a useful alternative source for alkalinity and it was suited for neutralizing spent acids.

By persevering, a market was eventually developed, but it also required the installation of a proper storage and bulk loading facility. Now most of the dust is sold for this purpose. Because the material competes with pure lime, it must be priced competitively and this means that there is a limit to how far it can be shipped. By any stretch of the imagination, it is not a money-making proposition.

At the present time, the demand for lime fines is not in balance with what is produced and we are looking for the market to expand. The field of industrial sludge solidification holds some promise.

Dr. J. Emery of Trow Limited has reported on sludge stabilization using lime kiln dusts. The results were promising. Lime can act as a drying and binding agent and it is reasonable to assume that sludge stabilization with steelmaking lime fines would give similar results. In order to be certain, testing would be required. The potential exists for diverting some lime fines to that type of operation in the future.

2. ACID REGENERATION IRON OXIDE DUST

This material is quite unique and it should be of interest as an example of secondary raw material and reuse situation.

First, why is there an iron oxide dust and why is it a particularly useful material?

Acids are used to clean steel. The removal of hard and brittle layers of iron oxide from the surface with acid is known as pickling, and at Hilton Works the job is done with hydrochloric acid. The acid dissolves the oxide and when the oxide is spent it is sent to the regeneration plant. In that process, acid and dissolved iron are separated. The acid is recovered and recycled while the dissolved iron is converted to a fine spherical iron oxide in the roasting step. The oxide is like jeweller's rouge and has been proven to be a valuable raw material for the electronic and pigment industry. The oxide is unique for the following reasons:

i) The chemical composition is constant. The consistency of the product is directly related to the chemistry of the steel. Since the grades of carbon steel are constant, the oxide chemistry varies little.

ii) The particle size distribution remains constant as well. Acid is regenerated by a method of spray roasting. Each droplet contains a finite amount of dissolved iron. Droplet size and the amount of dissolved iron is held constant so that when the liquid has evaporated each droplet leaves behind a similar amount of iron oxide.

iii) The oxide particles are small. 90% of the oxide is less than 10 microns in diameter. This is an advantage in handling the dust. It flows like water and can be conveyed pneumatically. As well, very little grinding is required in comparison to using iron ores for similar feed stock.

iv) Product purity is high with good colour consistency. The oxide is 98% Fe_2O_3 and is excellent feed stock for the ferrite industry. The material is used to manufacture recording tape and magnets.

This specialty market, however, has fluctuating requirements and not all of the oxide produced can be used. A larger demand would be beneficial. Occasionally some oxide has been used to produce iron chlorides for the water treatment trade, particularly for phosphate removal in sewage treatment plants. Generally speaking, oxide production is in balance with demand.

3. STEELMAKING IRON OXIDE DUST

The two previously cited cases are examples of steel plant by-products which are used by others as secondary raw material and nearly all of Stelco's production is reused. My last example, steelmaking iron oxide dust, does not fit as well. There is a potential for reuse, but reuse is an exception.

Iron oxide fume is generated in steelmaking processes such as open hearths and basic oxygen furnaces. At Hilton Works, furnaces are equipped with electrostatic precipitators to remove the oxide fume from furnace exhausts. About 400 tons of dust is collected daily. It is available to anyone and we are not likely to run out.

At Stelco, it cannot be recycled because the dust contains zinc and the size of the material is too fine. This problem is universal and the steel industry has studied recovery methods extensively. Unfortunately, no viable breakthrough has been reported. Here are some results:

i) Magnetic Separation of Iron Oxides and Zinc Oxides

Magnetic separation techniques are not feasible because the zinc is bound tightly to iron oxide. Recent studies by Dr. J. R. Porter of Lehigh University have confirmed that the zinc is present as a spinel and individual particles contain varying amounts of zinc.

More drastic approaches are required to dissociate the stable structure.

ii) Direct Reduction

The direct reduction technology was explored by Stelco and pilot studies have proven that most of the zinc oxide, namely 82 to 97%, can be removed. However, the process is not economical because of its high capital and operating cost.

iii) Marketing

Small quantities of steelmaking dust may be used for the following:

- A limited amount of dust has been used in the cement industry.
- Exploratory studies have identified uses in construction materials such as brick and tile.
- It may be useful as a drying agent for stabilizing industrial sludges.
- Small amounts might be used as mineral filters. The lack of colour consistency probably is a restriction.

I have touched on only a few of the opportunities which the steel industry presents when it comes to reusing steelmaking dust. However, there are many technical and economic problems which must be overcome before a substantial amount can be recycled internally. Internal use is the preferred goal because of the quantities involved. The oxide is a potential raw material, a source of iron oxide, and as such may be of interest to some of you and it is the main reason for mentioning it today.

. . .

LIME FINES

	%
Fe	1.2
SiO_2	1.2
CaO	64.8
MgO	25.8
MnO	1.4
Cr_2O_3	0.14
BULK DENSITY Lb/ft3	50
PRODUCTION Tons/day	5

STEELMAKING DUSTS

	OPEN HEARTH	BASIC OXYGEN FURNACE
PARTICLE SIZE % MINUS 400 MESH	80	50
BULK DENSITY LB/FT^3	38	60
PRODUCTION TONS/DAY	210	190
LB DUST/TON OF STEEL	52	54

ACID REGENERATION PLANT DUST

PARTICLE SIZE	90% < 10 microns 50% < 4 microns
BULK DENSITY Lb/ft^3	80
PRODUCTION	1000 tons/month

ACID REGENERATION PLANT DUST

	%
Fe_2O_3	97.80
SiO_2	0.001
CaO	0.22
MnO	0.36
Cr_2O_3	0.044
C	0.10
P	0.008
S	0.04
CuO	0.02
Cl^-	0.35

STEELMAKING DUSTS

	OPEN HEARTH %	BASIC OXYGEN FURNACE %
FE TOTAL	65.0	55.0
FeO	2.5	7.4
SiO_2	0.7	2.2
CaO	0.4	9.6
MnO	0.7	1.9
C	0.1	0.7
PbO	0.6	0.7
ZnO	2.5	3.7
S	0.3	0.2
CuO	0.6	0.4

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SYMPOSIUM

RECOVERY AND APPLICATIONS OF FILLERS FROM ASBESTOS MINE TAILINGS

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RECOVERY AND APPLICATIONS OF FILLERS FROM ASBESTOS MINE TAILINGS

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RECOVERY AND APPLICATIONS OF FILLERS FROM ASBESTOS MINE TAILINGS

Abstract

Asbestos mine tailings are accumulating at the rate of some 25,000,000 tons per year. These materials are described, and the recovery of fillers from these wastes is explained.

A new thermal treatment plant for producing fillers, under erection at Thetford Mines, Québec, si described. Some uses for the fillers produced by this plant are described, including:

Abrasive additive;
Composite latex roofing, and sheeting;
Reactive fillers in phenolics.

Biographical notes

Marcel Cossette graduated in Chemical engineering from McGill University. He began his career in the R & D Department of Asbestos Corporation Ltd. In 1966, he became Director of the QAMA Laboratory at Université de Sherbrooke. Since 1979, he has acted as Directeur, Recherche technologique of Société nationale de l'amiante (on a part-time basis).

MC/mjb
12/11/81

RECOVERY AND APPLICATIONS OF FILLERS FROM ASBESTOS MINE TAILINGS

Some 25 million tons of asbestos mining wastes are produced annually by the Canadian asbestos mines. Most of these consist of mill tailings produced by a dry extraction process. Over a billion tons are accumulated.

The size of particles range down from 5 cm, and most are below 1 mm. in. diameter. This material consists of ground serpentine rock (an hydrated magnesium silicate) with approximately five percent magnetite. Residual asbestos is also present. Some researchers have reported that as much as 40 percent may be in the form of asbestos fibre.

Fig. 1 shows the molecular structure of asbestos. This shows the hydroxyl groups that make up the top layer, and part of the penultilate layer. These can be driven off by heating to form two minerals: forsterite and enstatite. Both of the latter are magnesium silicates with ratios of magnesia to silica that are different from each other, and from serpentine minerals. In particular, it has been established that roasting the tailings one hour at 900°C yields non toxic products. This fact then is the basis for producing fillers from asbestos mine wastes.

Production

The Société nationale de l'amiante has decided to erect a demonstration plant with a theoretical capacity of 7,000 t/a to test the markets for such fillers. The plant went on stream in August of 1981 and production is gradually approaching rated capacity.

The plant is fed by one particular stream of tailings from the Bell Mines asbestos mill. This consists of dry -27 Mesh material. This is transported by means of a bulk transporter equipped with self discharge equipment allowing rapid unloading with zero dust emissions.

The material is received in a bin fitted with a live-bottom discharge mechanism and fed to a rotary kiln. This kiln has an internal diameter of 5 ft and a length of 40 ft. Fuel oil is burned pending the arrival of natural gas, compressed air is used to atomise the fuel. Temperatures up to 1300°C cam be attained.

The usual operating conditions keep the mineral at 900°C for one hour. Then it discharges into a rotary cooler with a double shell. Cold air is drawn first through the annulus, thus cooling the inner wall, and then the air is drawn through the central core to cool the product by direct contact. The heated air is used to fire the kiln. The kiln discharge gas is cooled by dilution with cold air, and is dedusted in cyclone collectors, and filter bags. The dust collected is recycled to the kiln feed.

The roasting reduces the particle size to around -30 Mesh. If finer products are desired the product is classified on rotex screens. The oversize material is ground in Babcock & Willcox roller mills equipped with internal air classifiers.

The discharge of the mills is collected in cyclone collectors, and bag filters.

The final products are bagged in multiwall paper bags of 30 kg each.

Applications

The coarsest products (-30M) are being tried in floor tiles. In this application, it is apparent that the asbestos skeletons, referred to as pseudomorphs, seem to offer some reinforcement not obtained from ground limestone.

This product is also used in fertilizers as a source of magnesium. This size of product is also used as a foundry sand. It is less soluble in various ferrous metal alloys than silica. It also provides smooth castings requiring no additional finishing.

Finer grades are used in fluid bed furnaces for the combustion of difficult to burn organic materials. The particle size distribution must be narrow to prevent the loss of fines. The heat resistance must be high. One role of the filler is to act as a heat transfer agent.

Still finer grades (-100M) are used for scrubbing sulfur out of smoke. This process is still under development.

Grades below 150 Mesh are used as filler in phenolics where as much as 90 percent filler with 10 percent resin can yield high performance products.

Another use for these is as filler in roofing paper where it promotes dimensional stability in humid environments.

The finest product (-200M) is used as a filler in latex bound felts for vinyl cushion flooring. It imparts hot tensile strength.

Still finer products are contemplated, but a suitable grinding unit will have to be installed before this becomes available.

Conclusion

Several potential markets appear to be firming up for these products. If some of the markets should be proven, then a large scale industrial plant will be erected.

The present cost target is $60/ton.

If anyone sould be interested in trying these materials they are invited to communicate with the author.

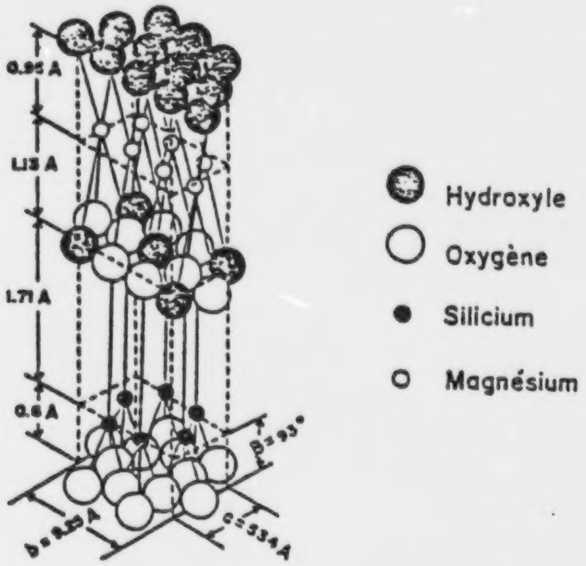
0.95 A
1.13 A
1.71 A
0.6 A
β=93°
b=9.25A
c=5.34A
Hydroxyle
Oxygène
Silicium
Magnésium

Fig. 1 Unit cell in the crystalline structure of chrysotile (after Cossette, Lemonde and Massey. L'Union Médicale Can 100 759 1971).

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FILLERS IN RUBBERS

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FILLERS IN RUBBERS

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for presentation to the
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INTRODUCTION

Fillers are used in rubber to improve physical properties such as strength and stiffness, to provide colour, aid in processing, and to reduce cost.

Inorganic materials are more widely used than organic materials as fillers and are generally classified into two groups, i.e. reinforcing fillers or non-reinforcing fillers. The principal reinforcing fillers for rubber are small particle size carbon black made by pyrolysis of hydrocarbons and fine silica dust made by the fuming of silicon chloride. The addition of carbon black or silica to natural or synthetic elastomers markedly increases tensile strength and modulus of the resultant composite. Carbon black is the reinforcing filler most widely used since it is relatively inexpensive and easy to process. Silica is used when a non-black, coloured product is desired or special properties such as cut-resistance are required.

In order for a filler to reinforce the physical strength, stiffness and toughness of a rubber compound, it must exhibit small average particle size, have a fibrous shape factor (aspect ratio L/D of greater than 3:1), be well dispersed and interact chemically with the matrix elastomer.

In general, mineral fillers which are prepared by grinding processes are of larger sized particles of roughly spherical shape and exhibit little direct interaction with the matrix elastomer. Thus, these mineral fillers tend to be non-reinforcing.

There is a wide variety of inorganic materials and minerals used in the compounding of rubber products, some of which are listed in Table I. Although these are considered non-reinforcing fillers, they do provide a range of other specific properties and processing advantages for rubber compounds and products.

Some specific properties are:

- reduced cost
- colour variety
- specific gravity
- flame resistance
- acid neutralization
- reduced gas permeability
- heat resistance
- electrical resistivity or conductivity
- lower heat build-up in dynamic applications
- sound attenuation.

Some processing advantages:

- less energy required in mixing
- smoother extrusions and mouldings
- reduced sticking to mills
- easier mould release
- reduced blocking
- easier calendering.

CLAY AS A FILLER FOR RUBBER:

The mineral used in largest quantity as a filler in rubber is kaolin (hydrated aluminum silicate) derived from clay. There are two processes used in the production of rubber-grade clays: (i) dry grinding with air flotation, and (ii) water fractionation, followed by filtration, drying and grinding.

Rubber grade clays are also classified as "hard" and "soft". Hard clays produce rubber compounds characterized by high modulus, high tensile strength, good resistance to abrasion, high cured stiffness, and high viscosity in the unvulcanized state. Soft clays give compounds with lower modulus and tensile strength, poorer abrasion resistance, lower vulcanized stiffness, and lower unvulcanized viscosity.

The differences are due primarily to differences in particle size. Hard clay has plus 85% finer than 2 microns, while soft clay has a maximum of 60% finer than 2 microns.

An example of the differences between hard and soft clay at a 150 phr loading in natural rubber is as follows:

	Hard	Soft
Tensile Strength (psi)	2800	2400
300% Stress (psi)	2300	1860
Hardness "A"	73	68
Moorey Viscosity, ML-4 @ 212°F	47	34

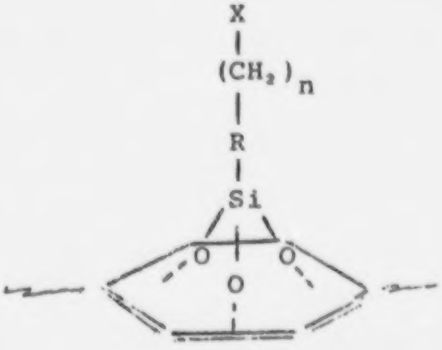
This comparison indicates that higher loadings of soft clay would be possible with little change in processibility and would give lower cost compounds.

In some low cost EPDM rubber compounds (e.g. carpet tile backing) as much as 375 phr soft clay can be used in combination with 100 phr FEF carbon black and 150 phr oil.

Another class of clays used by the rubber industry are calcined clays. Kaolin clays contain approx. 14% water of hydration. When this water is removed by calcining, a distinct improvement in colour is obtained and a decided improvement in rubber compound properties is obtained. Calcined clays also provide good compression set resistance, and are used by the rubber industry in wire and cable insulations, where they provide excellent wet electrical resistance properties. Other uses are in tire white sidewalls and other white rubber products.

CHEMICALLY MODIFIED CLAY:

The surface of kaolin particles is essentially inert and does not react with elastomers. Thus, in order to improve the reinforcing properties of clay, it is necessary to generate a chemical interaction between the filler particles and rubber matrix. A unique family of organofunctional silanes have the ability to react both with the surface of kaolin particles and the rubber matrix, thus providing a chemical bond between the filler and rubber. Such compounds are known as "coupling agents" and lead to enhancement of the composite's strength and modulus properties. Typical useful coupling agents are mercaptopropyl (trialkylsiloxane) and aminoalkyl (trialkylsiloxane). It is theorized that the alkylsiloxane groups of the coupling agent can condense with the silanol functional groups of the filler, and the mercaptan function can react with the hydrocarbon elastomer matrix. The amino-functional coupling agent is more effective in chlorinated polar and urethane elastomers.



X = $-SH$

$-NH_2$

$-RCH = CH_2$

For example, polyisoprene rubber filled with kaolin, modified with mercaptopropylsilane coupling agent, exhibits a significant increase in modulus, hardness and tear resistance over that for compounds with unmodified kaolin. This can be attributed both to better matrix/filler interaction and filler dispersion.

COMPARATIVE TEST DATA
(75 phr filler in Natsyn 400)

	Unmodified Kaolin	Mercaptosilane (1.5%) on Kaolin
Modulus, 300%, psi	770	1770
Tensile Strength, psi	3080	3240
Elongation, %	580	480
Hardness, Shore A	58	65
Compression Set, B, %	30	14

Die C, tear, ppi	155	235
Mooney Scorch, min (MS-3/250°F)	18	23
Mooney Viscosity (ML-4/212°F)	33	42

Property improvements in rubber compounds containing chemically-modified clay are:

- higher modulus
- lower hysteresis (low heat generation)
- better abrasion resistance
- lower compression set
- better aging characteristics

Thus, this chemical modification of clay allows it to be used in more demanding applications, such as:

- white tire sidewall and coloured compounds
- tire carcasses and under treads
- V-belts
- motor mountings
- vibration dampeners
- industrial rolls
- neoprene masking compounds
- neoprene latex gloves
- caster wheels
- urethane automotive brake components.

GENERAL APPLICATIONS OF CLAY IN RUBBER PRODUCTS:

Hard clays give excellent resistance to abrasion in comparison with other rubber pigments. Therefore, clay is used extensively in all non-black rubber goods where wear is of importance. Notable examples are heels, soles, tiling, flooring, matting, footwear, conveyor-belt covers, bicycle tire treads, etc. Hard clays impart stiffness to uncured rubber compounds. This property is important for good processing in the manufacturing of hose, tubing, jar rings, extruded automotive rubbers, etc. Clay also aids in the elimination of moulding difficulties due to stock 'mushiness', thereby finding wide application in moulded goods such as drug sundries, household goods, toys, novelties, etc. Other applications of hard clay in rubber are in such articles as insulated wire, gloves, proofed goods, adhesives, tire treads, butyl inner tubes, etc.

When it is desirable to use high loading to reduce cost and when good abrasion resistance is not paramount, soft clays are used, e.g. in tire tread wire insulation, bicycle tire carcass compounds, household goods, proofed goods, blown sponges, toys, novelties, etc.

Water-fractionated clays are substantially free from mica and find application in articles such as small tubing, refrigeration gaskets, and insulated wire by the continuous vulcanization process.

MINERAL FILLERS OTHER THAN CLAY:

Listed below are some processed mineral fillers often used in rubber compounds.

Filler	Uses and Advantages
Aluminum hydroxide (hydrated)	Reinforcing filler in shoe soling and in mechanical goods. Gives high tensile strength, elongation, tear strength, dielectric strength.
Antimony Trioxide	Semi-reinforcing filler used in flame-resistant compounds.
Barytes (barium Sulphate)	Most used to reduce cost, in chemical resistant tank lining, in high density materials, V-belts, flat belts, mats, matting,

	moulded and foam goods, O-rings, oil seals, friction tape and sundries.
Magnesium Carbonate	Reinforcing fillers - gives high tensile strength, tear and abrasion resistance. Used to stiffen uncured extruded products, cycle covers, used in highly resilient stock. Gives highly resilient stocks even when highly loaded.
Magnesium Oxide	Light grade - used as acid acceptor (curative) in halogen-containing polymers. Heavy grade - heat resistant compounds used in seals and gaskets.
Mica	Laminar type filler imparting good heat resistance and low permeability to gases.
Talc (hydrous magnesium calcium silicate)	Dusting agent. Filler and extender for most rubber compounds and latex foam. Used in tires, tubes, rolls, moulded and extruded products, sundries, heat resistant products such as gaskets, autoclave jointing, etc.
Titanium Dioxide	Reinforcing filler used mainly for its whitening power in tire sidewalls, hospital accessories, floor tiles, and as an excellent heat resistant filler for silicone rubber.

Whiting (calcium carbonate)	Used mainly to reduce cost. Can be used in very high loadings. Gives compounds a moderate hardness but poor tensile strength and tear resistance. Used almost universally in rubber footwear. Also used in rubber wire and cable coatings, moulded and extruded mechanical, sport, automotive and household goods.
Zinc Carbonate	Cheaper replacement for titanium dioxide, although not as effective. Used as a neutral acid acceptor in halogen-containing polymers.
Zinc Oxide	Densifying agent for golf balls.

DIFFICULTIES IN USING MINERAL FILLERS:

Because of their different surface chemistry from carbon black, many inorganic filler materials inhibit the normal cure of rubber compounds and prevent development of the desired physical properties. These problems are particularly troublesome with peroxide cures since acidic residues interfere with the cure chemistry. Thus, other additives and unique compound formulations must be developed for each filler and rubber composition.

FUTURE OUTLOOK:

With rising costs for petroleum feedstock and energy, the conventional rubber fillers, carbon black and silica, will continue to rise in price to a considerable premium over some mineral materials. Also, as grinding and refining techniques for minerals improve, and lower cost coupling agents are found, mineral fillers will play an increasingly important role in rubber compounding in the future.

TYPES OF INORGANIC AND MINERAL FILLERS USED IN RUBBER

Silicates:
- clay
- talc
- mica
- asbestos
- feldspar
- bentonite clay
- wollastonite
- fuller's earth
- pumice
- pyrophillite
- rottenstone
- slate flou
- vermiculite
- calcium silicate (precip)
- magnesium silicate (precipitated)

Oxides:
- aluminum oxide
- hydrated alumina
- antimony trioxide
- magnesium oxide
- titanium dioxide
- zinc oxide
- silica
  - quartz
  - diatomaceous earth
  - tripoli
  - pyrogenic
  - hydrogel and aerogel

Carbonates:
- calcium carbonate
  - precipitated
  - ground limestone (whiting, chalk)
  - ground marble
- barium carbonate (precipitated)
- magnesium carbonate (precipitated)

Sulphates:
- barium sulphate
  - barytes
  - blanc fixe
- calcium sulphate

Hydroxides:
- calcium hydroxide (lime)
- magnesium hydroxide

Carbon:
- carbon black
  - furnace
  - lampblack
  - acetylene
  - channel
  - thermal
- graphite
- fibres

Metals:
- powders
  - copper
  - aluminum
  - bronze
  - lead
  - zinc
  - steel
- fibres
- whiskers
- wire

Miscellaneous:
- barium ferrite
- magnetite (ferrous-ferric oxide)
- molybdenum disulphide
- glass
  - fibres
  - flakes
- ground

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SYMPOSIUM

THE ROLE OF MINERAL FILLERS IN PIGMENTED COATINGS

G.G. DAVIS

GLIDDEN COMPANY
TORONTO, ONTARIO

THE ROLE OF MINERAL FILLERS IN PIGMENTED COATINGS

MINERAL FILLERS

1. ECONOMIC ROLE OF FILLERS
2. SPECIALTY PIGMENTS
3. PROCESSING OF MINERAL PIGMENTS
4. SPECIFICATIONS
5. COATING INDUSTRY AS A CONSUMER

THE ROLE OF MINERAL FILLERS IN PIGMENTED COATINGS

Gerald G. Davis

GLIDDEN COMPANY, Division of SCM (CANADA) Limited

* * * * * * * * * * * *

Protective coatings serve a variety of purposes amongst which, decoration and protection of structural materials are most important. They are complex chemical mixtures, usually composed of from 10 to 20 components drawn from an inventory of more than 1000 raw materials. They are called upon to meet exacting specifications, not only with respect to these benefits, but as well with respect to their application characteristics and storage stability.

Within this framework, extender pigments, of which mineral fillers are an important class, serve to reduce the cost of the paint, without disturbing the critical balance of the other components. These pigments may serve, as well, to improve certain properties of the paint, or the dry film.

In addressing the economic benefits of fillers, it is important to realize that paint is sold on a volume basis and that cost reduction is effected by replacing resin solids with extender pigments. Table 1 shows that a savings of between $3.50 and $4.00 accrues when a gallon of resin solids are replaced by a gallon of filler in a batch of paint.

In practice, this equates to a material savings of $0.22 per gallon in the formulation of a semi-gloss alkyd paint, as shown in Table 2.

This may not seem a great deal, but the savings to the consumer may be 4 to 5 fold this amount, taking into account the retail price structure.

There is one other economic advantage of note and that has to do with the use of calcined clay to contribute to hiding in flat paints. In this application, the clay replaces some of the opaque pigment rutile titanium dioxide. Table 3 shows that a savings of about $27.50 accrues when a gallon of calcined clay replaces a gallon of titanium dioxide in a batch of flat paint. Comparing two flat latex paints, as in Table 4, having equal hiding and other properties where three gallons of the titanium dioxide has been replaced with calcined clay per 100 gallons, shows an $0.88 per gallon savings.

This is a considerable cost saving, and it is even more striking when one realizes that calcined clay in itself is transparent, when completely wetted by the vehicle, as shown in Figure 1. The reason for this is that opacity, which derives from light scattering is very dependent on the difference in refractive indices between the pigment and its surrounding environment. The relevant indices are presented in Table 5, where it can be seen that calcined clay has the same refractive index as most resins, and hence, gives transparent films.

The large difference in refractive indices between titanium dioxide and these binders accounts for the great hiding quality of this pigment. In flat paints, the pigment volume concentration is so high that the film becomes porous and scattering occurs at the pigment/air interface, where there is a sizeable difference in refractive index. Calcined clay is the preferred pigment for this role because of its microporous structure which gives a large air to pigment interface.

Apart from their cost reduction function, low cost mineral extenders may serve as well to reduce gloss and control angular sheen in flat and semi-gloss paints. They also find some purpose in oil based paints in the development of rheology for improved application and storage stability. However, where mineral pigments are incorporated to improve, or provide a particular performance property of the applied film, special grades are required, and the cost considerations previously addressed no longer apply. As a case in point, lamellar pigments, such as mica, provide a reinforcing action in paint films, thus improving exterior durability. This same pigment arranges itself in overlapping layers, producing a very effective vapour barrier and thus, finds considerable use in primer sealers. Table 6 shows that mica pigment costs $11.80 per gallon, or almost double the cost of resin solids; and accordingly, its use is accompanied by a considerable increase in the cost of the paint.

These pigments are obtained from soft rocks, or deposits and are processed by crushing, grinding, and classification, as shown in Table 7. The grinding process may be dry in which case, the material is powdered in a hammer mill, or a roller mill and classified by air floatation. In a wet grinding process, a slurry of the crushed rock is ground in a ball, or pebble mill and then classified in hydraulic classifiers, or by centrifugation. The slurry is then filtered and dried. In some cases, these products are further micronized; however, the low price of extenders places a limit on the extent to which further refinement can be warranted.

The above notwithstanding there is still a broad range of qualities available within a given class of fillers, as shown in Table 8.

In terms of the specifications established by the paint industry for mineral extenders, it is perhaps best to look at a typical specification for calcium carbonate, (Table 9). Other things being equal, the higher the bulking value, the more attractive the pigment as a cost extender. In like manner, a low value for oil absorption, which gives a measure of the amount of resin required to wet the pigment, is desireable since it allows for incorporation of considerable pigment, without loss of film integrity.

Dry brightness is important, since light pastel colours make up the bulk of paint sold. In some cases, it is necessary to resort to chemical bleaching to attain an acceptable brightness level. A low content of water soluble salts is desirable from the point of view of emulsion stability. Most mineral pigments slurries have a pH in the range of 4.0 to 8.0. As regards particle size, the key specification is that there be no residue after screening with a 325 mesh screen.

In assessing the importance of the coating industry as a consumer of filler pigments, the statistics for the United States market, as shown in Table 10, are perhaps most important. Note that the three pigments: Calcium Carbonate, Talc, and Clay, represent 71% of the total market. Another feature of interest is the relatively flat growth pattern, which is a reflection of the American Architectural Finishes market, which has an annual growth rate of about 1.7%.

The Canadian market follows a close parallel with 75.4% of the filler volume in the three basic pigments, as shown in Table 11. Likewise, the volumes of both filler and paints, as collected in Table 12, have the same pattern as the U. S. market, with slightly higher growth rates. One bright spot on the horizon for Canadian producers is the growing adoption of Canadian sourced fillers, in preference to fillers, traditionally supplied by U. S. producers. Table 13 reflects this growing change for the Glidden Company.

In summary, mineral filler pigments are used in the coatings industry, principally as a means of reducing the material costs of paint. To the extent that the paint market is a mature market, the consumption of these pigments can be expected to maintain a flat growth curve in a very cost-competitive environment.

TABLE 1

COST PER GALLON OF COMMON MINERAL FILLERS AND RESINS

COMPONENT	COST PER GALLON (DOLLARS)
CALCIUM CARBONATE	2.30
TALC	2.80
SILICA (CRYSTALLINE)	2.74
SODIUM POTASSIUM ALUMINUM SILICATE	1.87
ALKYD RESIN SOLIDS	6.40
VINYL ACRYLIC LATEX SOLIDS	6.20

TABLE 2

SEMI-GLOSS ALKYD PAINTS

COMPONENT	PAINT #1	PAINT #2
	GALLONS	
RESIN	67.1	78.4
TITANIUM DIOXIDE	6.9	6.9
CALCIUM CARBONATE	7.5	---
TALC	1.0	---
DIATOMACEOUS SILICA	---	1.1
SOLVENT	14.7	11.0
OTHER CHEMICALS	2.8	2.6
TOTAL	100.0	100.0
RAW MATERIAL COST	$508.00	$530.00
RM COST PER GALLON	$ 5.08	$ 5.30

TABLE 3

COST ADVANTAGE OF CALCINED CLAY FOR DRY HIDING

PIGMENT	COST/GALLON
TITANIUM DIOXIDE	33.00
CALCINED CLAY	5.44

TABLE 4

FLAT LATEX PAINTS

COMPONENT	PAINT #1	PAINT #2
	GALLONS	
Vinyl Acrylic Emulsion	28.95	28.95
Titanium Dioxide	14.23	11.05
Calcined Clay	0	3.12
Water	49.54	49.54
Coalescent	3.05	3.05
Freeze Thaw Stabilizer	1.29	1.29
Additives	2.94	3.00
	100.00	100.00
Pigment Cost Per 100 Gallons	$469.59	$381.62

Savings Per Gallon = $0.88

TABLE 5

REFRACTIVE INDICES

RESINS	∽ 1.6
RUTILE TITANIUM DIOXIDE	2.7
CALCINED CLAY	1.6
AIR	1.0
WATER	1.3

TABLE 6

MICA

PHYSICAL MECHANICS

1. THIN PLATES LEAF PARALLEL TO SURFACE OF PAINT FILM
2. ASPECT RATIOS AS HIGH AS 25 TO 1
3. TOUGH AND FLEXIBLE
4. MOISTURE AND HEAT RESISTANT

BENEFITS

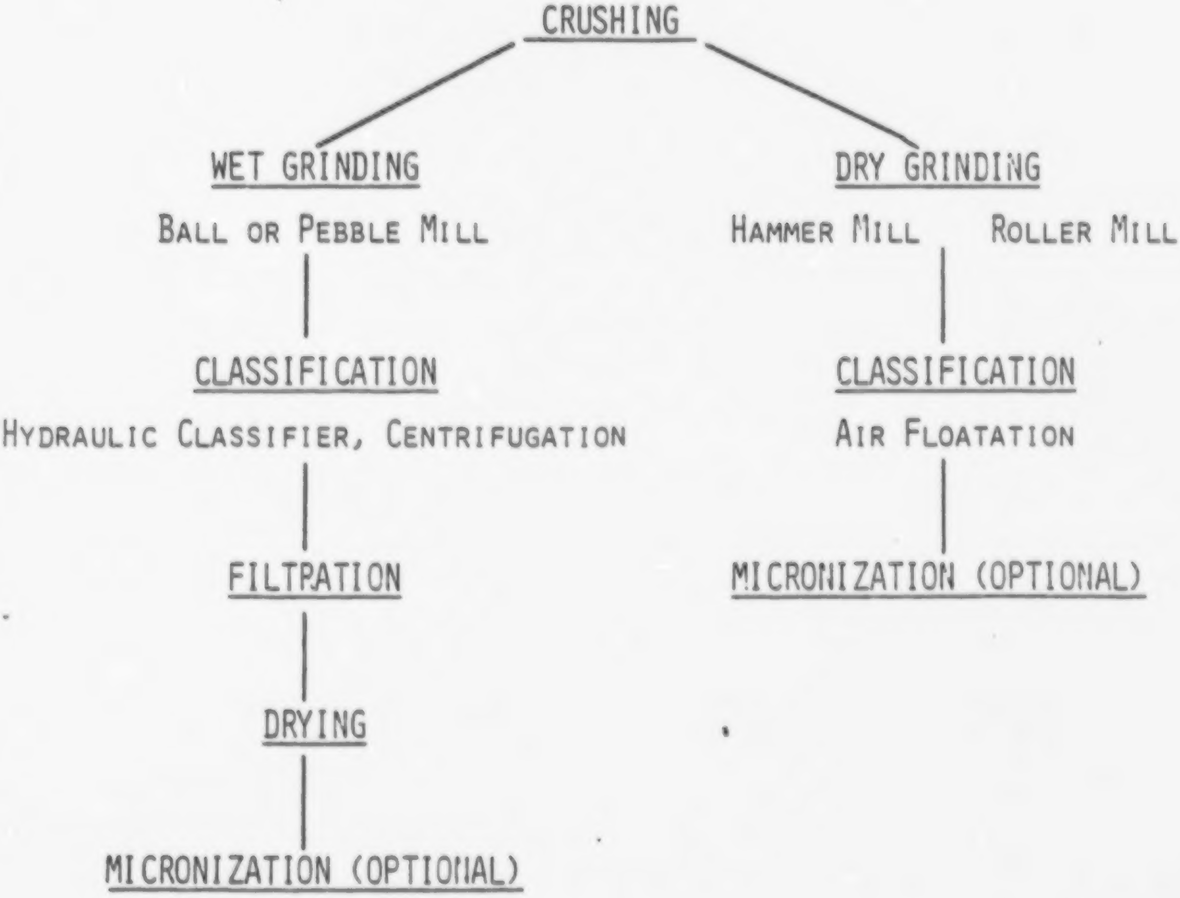
1. STRESS RELIEF - MINIMIZE CHECKING AND CRACKING, ADHESION
2. VAPOUR BARRIER
3. CORROSION RESISTANCE

COST PER GALLON

MICA	$11.80
RESIN SOLIDS	$ 6.30

TABLE 7

MINERAL PIGMENT PROCESSING



CRUSHING

WET GRINDING

BALL OR PEBBLE MILL

CLASSIFICATION

HYDRAULIC CLASSIFIER, CENTRIFUGATION

FILTRATION

DRYING

MICRONIZATION (OPTIONAL)

DRY GRINDING

HAMMER MILL ROLLER MILL

CLASSIFICATION

AIR FLOATATION

MICRONIZATION (OPTIONAL)

TABLE 8

CLAY PIGMENTS

1. WATERWASHED DELAMINATED CLAYS

GRADE	BRIGHTNESS	OIL ADSORPTION	PARTICLE SIZE
A	+	+	LARGE
B	++	+	MEDIUM
C	+	++	FINE PARTICLE

2. WATERWASHED CONVENTIONAL CLAYS

GRADE	BRIGHTNESS	OIL ADSORPTION	PARTICLE SIZE
A	--	=	COARSE
B	--	+	FINE
C	+	+	FINE
D	++	++	VERY FINE

3. CALCINED CLAYS

GRADE	BRIGHTNESS	OIL ADSORPTION	PARTICLE SIZE
A	+	+	MEDIUM
B	++	++	MEDIUM - FINE

SOURCE: PAINT REDBOOK 1979

TABLE 9

TYPICAL SPECIFICATION FOR MINERAL PIGMENT

CALCIUM CARBONATE

PROPERTY	VALUE
BULKING VALUE, GALLONS/100 LBS.	3.70
OIL ABSORPTION	15 - 17
DRY BRIGHTNESS	95% MINIMUM
WATER SOLUBLE SALTS	0.07%
RESIDUE ON 325 MESH SCREEN	NONE

TABLE 10

CONSUMPTION OF SELECTED PIGMENTS BY U. S. COATINGS INDUSTRY

1974 - 1977

MILLIONS OF POUNDS

MINERAL PIGMENT	YEAR 1974	1975	1976	1977
CALCIUM CARBONATE (NATURAL)				460
TALC	316	281	378	400
CLAY	280	229	300	330
BARYTES	96	70	99	110
MICA	67	46	55	65
GROUND SILICA				112

TOTAL CONSUMPTION 1977 = 1.6 BILLION POUNDS

= $119,000,000

SOURCES: MINERAL YEARBOOK
C. H. KLINE & COMPANY

TABLE 11

FILLER PIGMENT USAGE : CANADA 1978

EXTENDER PIGMENT	% OF TOTAL
NATURAL CALCIUM CARBONATE	45.2
TALC	18.7
CLAY	11.5
NATURAL SILICAS (GROUND)	4.4
MICA	2.4
ALL OTHER	17.8

SOURCE : STATISTICS CANADA CATALOGUE 46-210 ANNUAL

TABLE 12

MARKET STATISTICS : FILLER PIGMENTS

CANADA

YEAR	PHYSICAL VOLUME LBS. ('000)	DOLLAR VOLUME $('000)	TOTAL SHIPMENT OF SELECTED PAINT PRODUCTS GALS. ('000)
1978	158,809	11,394	64,448
1977	147,410	9,081	63,534
1976	165,517	9,321	59,971
1975	130,094	7,358	60,849
1974	129,425	6,390	58,056

AVERAGE PHYSICAL VOLUME GROWTH - FILLER PIGMENTS = 5.5%

- ARCHITECTURAL FINISHES = 2.8%

SOURCE: STATISTICS CANADA CATALOGUE 46-210 ANNUAL

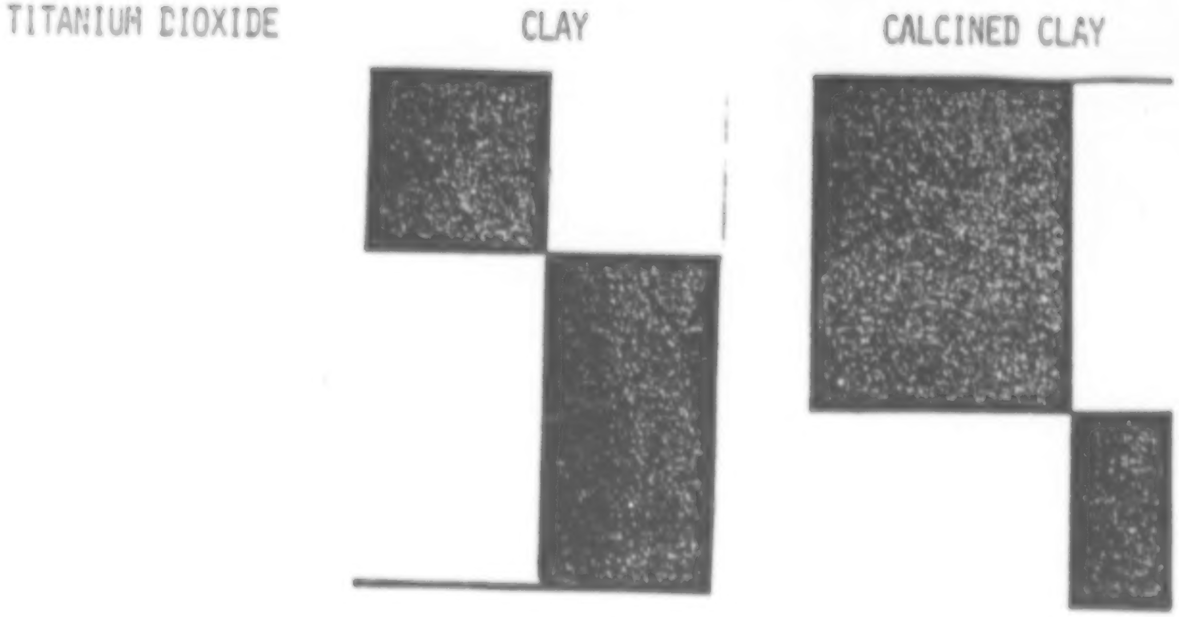
TABLE 13

MINERAL EXTENDER PIGMENTS USED IN GLIDDEN PRODUCTS

YEAR	CANADIAN SOURCED	U.S. SOURCED
1978	21%	79%
1980	59%	41%

FIGURE 1

HIDING POWER OF CLAY


TITANIUM DIOXIDE
CLAY
CALCINED CLAY

FILMS AT EQUAL PIGMENT VOLUME CONCENTRATIONS

ONTARIO RESEARCH FOUNDATION

CANMET

SYMPOSIUM

FILLERS FOR PLASTICS

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FILLERS FOR PLASTICS

by

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August 1981

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INTRODUCTION

Except for a few special applications, most plastics employ fillers to reduce the manufacturing costs and or improve performance. It is interesting to note that calcium carbonate commands more than 60% of the total filler market, and that the five filler types listed in Table 1 represent over 90% of the total market for fillers. Recent forecasts predict a rather spectacular growth in the use of such fillers during the next twenty years (1), resulting in a 6-fold increase in filler usage by year 2000 (see Figure 1).

It is generally assumed that fillers are less expensive than the resin although as Tables 1 and 2 indicate, filler costs vary greatly depending upon the quality, fineness and surface treatment and may even exceed or be comparable to the cost of the resin. In those cases where the filler cost is dominant the incentive is usually property enhancement. It is seldom, however, that all the desirable properties of the composite are enhanced and so the final balance of properties tends to be a compromise. For example, most fillers when added to a resin increase the modulus and stiffness substantially but usually at the expense of fracture toughness, thereby limiting the amount of filler that may be incorporated into the product.

Fillers may be divided into three categories according to their particle shape, that is, spherical, fibrous or flake, where the spherical category includes all particulate fillers that have no dominant dimension. The influence of particle shape on the mechanical properties is depicted in Figures 2 and 3 for a glass filler in a typical resin. In order to obtain these values, both the glass fibers and the glass flakes have been assumed to be greater than their critical pullout dimensions. The particulate (spherical) values include all fillers having size ranges greater than one micron, that is, non-reinforcing types. Note that the calculations are predicated upon isotropic properties in a plane, a situation which is relevant to many molded products. Based upon these calculations, flake-type fillers would appear to be more efficient as reinforcing agents when compared to spherical or fibrous type fillers. However, there are a number of reasons why flake-type fillers have not yet attained greater commercial acceptance. The first reason may be attributed to the lack of flake-type fillers having dimensions in excess of their critical pullout ratios, that is, flakes having large diameter to thickness ratios. This important characteristic is commonly referred to as the flake "aspect ratio" and has the same influence on properties as the aspect ratio of a fibrous filler.

In most flake composite systems the flake aspect ratio should be in excess of 30 in order to impart significantly greater modulus and/or strength. This is demonstrated in Figure 4 for a polyester resin system containing mica flakes where the volume fraction of mica is constant at 50%. Unfortunately, most finely ground mica fillers have mean aspect ratios less than 30 so that the desired enchancement in composite properties cannot be achieved with such fillers. Talc and clay fillers have aspect ratios less than 30 so that their performance leans more towards the behaviour of particulate or spherical type fillers in resins.

Even when flakes of greater aspect ratios are available, there are problems associated with mixing, dispersion and coupling. The ultra-thin, high aspect ratio mica flakes are easily broken during processing so that special techniques must be employed to ensure that the high aspect ratio is preserved in the final product. Encapsulation, low shear processing and runnerless, valve-gated injection molding are just some of the techniques which have been successfully employed with flakes to achieve improved mechanical properties in the resulting composite. More recent investigations involve new processing aids, coupling agents and special processing methods which encourage flake overlap and parallel orientation. These modifications may eventually permit the attainment of levels of reinforcement predicted by theory (2,3).

THE SZEGO MILL

The cost of producing fine fillers by grinding techniques tends to increase exponentially as the resulting particle size becomes smaller. The quality of the filler is also dependent upon the particle size distribution and in most applications this requires that the packing efficiency should be as great as possible. At the University of Toronto, Trass and co-workers (4,5) have developed an energy efficient grinding mill which is designed to produce fine fillers with a controlled particle size distribution in the 10 micron region. This grinding mill was an outgrowth of the pioneering studies conducted by Szego (6). This compact mill comprises a stationary, cylindrical grinding surface inside of which a number of helically grooved rollers rotate at high speed. The coarse ore may be fed by gravity and discharged through the bottom as illustrated in Figures 5 and 6. The radial pressure of the rotors exerts a crushing action which reduces the coarse aggregate to a fine particle size which can be controlled by the mass and rotational speed of the rotors. Helical grooves in the rotors aid in the smooth transport of material through the grinding zone. This mill has successfully ground coal in oil to produce a stable colloidal suspension for use as an economical fuel for burners (4,6).

PARTICLE CLASSIFICATION

The particle size distribution of a filler frequently needs to be adjusted in order to optimise the packing efficiency. In the case of fibrous or flake type fillers, classification may be desirable to isolate a particular size or aspect ratio. For filler particle sizes in the 50-230 micron range, the Infrasizer or Tervel Separator (a laminar air classifier) has been employed to fractionate particles on the basis of settling (terminal) velocity into several fractions (7).

The technique of optimizing the packing efficiency by modifying the particle size distribution has been described by Ferrigno (8).

In the case of flakes it would be preferable to isolate particles having similar thicknesses or aspect ratios rather than selection based upon diameter (sieving) in order to maximize the reinforcement capability. The Tervel Separator permits the selection of any combination of flake diameters and thicknesses by subsequent sieving of the air classified fractions. However, this approach is complex and is restricted to particles greater than 50 microns. Current efforts are directed at producing controlled diameter/thickness distributions directly by improved grinding techniques such as ultrasonic comminution (9).

SURFACE MODIFICATION OF FILLERS

As particle sizes become smaller, the problems of dispersion become greater. The use of surface active compounds, for example metal stearates, organo-titanates, or chlorinated paraffins can aid dispersion and reduce the energy requirements for mixing and processing. If the dispersing agent also provides a physical or chemical bond between the filler surface and the polymeric matrix then it also becomes a coupling agent and may enhance the mechanical properties through improved stress transfer between the two phases. Silanes are almost exclusively used as coupling agents for glass or silicate type fillers since the silanol group provides a strong water impervious chemical bond to such chemically similar surfaces. However, silanes are not unique in this respect and in special circumstances many organometallics (e.g. chromium complexes, titanates) can function effectively as adhesion promoters at filler interfaces.

A good coupling agent however, may not function as an efficient dispersion aid;nor does a good dispersing aid necessarily imply good coupling. Dispersing aids enhance flow properties and provide lubrication during processing, thereby encouraging sizeable increases in production rates without incurring corresponding increases in processing energy. The trend towards finer particle sizes will make the task of mixing and dispersion much more difficult so that processing aids or surface modification may become more essential for satisfactory performance. Consequently, the future development of filler technology should see greater emphasis on the production of surface-treated fillers. An added benefit of such surface treatment is reduced dust formation (a potential health hazard) and increased bulk densities (compaction).

CONCLUSION

The use of fillers in plastics is expected to increase at an annual rate of 10% and reach a volume of 16 million tonnes by year 2000, representing a 6-fold increase in less than 20 years. Future emphasis will be directed at the production of finer filler particles at lower cost by means of more efficient grinding and classification methods. Filler producers will need to become more familiar with surface treatments as the market becomes more competitive. Fillers such as mica offer considerable potential for improvement if grinding techniques can be developed to produce high aspect ratio flakes at lower cost.

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TABLE 1.

FILLERS FOR THE PLASTICS INDUSTRY
1980

Filler	Volume 1,000 metric tonnes	Price $/m³
Calcium carbonate	1,500	240 - 1500
Asbestos	350	260 - 1100
Talc	200	90 - 280
Aluminum trihydrate	200	320
Mica	100	400 - 1100
Miscellaneous	250	—
TOTAL	2,600,000 tonnes	

TABLE 2.

RESIN PRICES

	Median Price (1980) $/m³
Polyethylene	880
Polypropylene	830
Polyester (unsaturated)	1400
Nylon 66	3400
Polycarbonate	3200

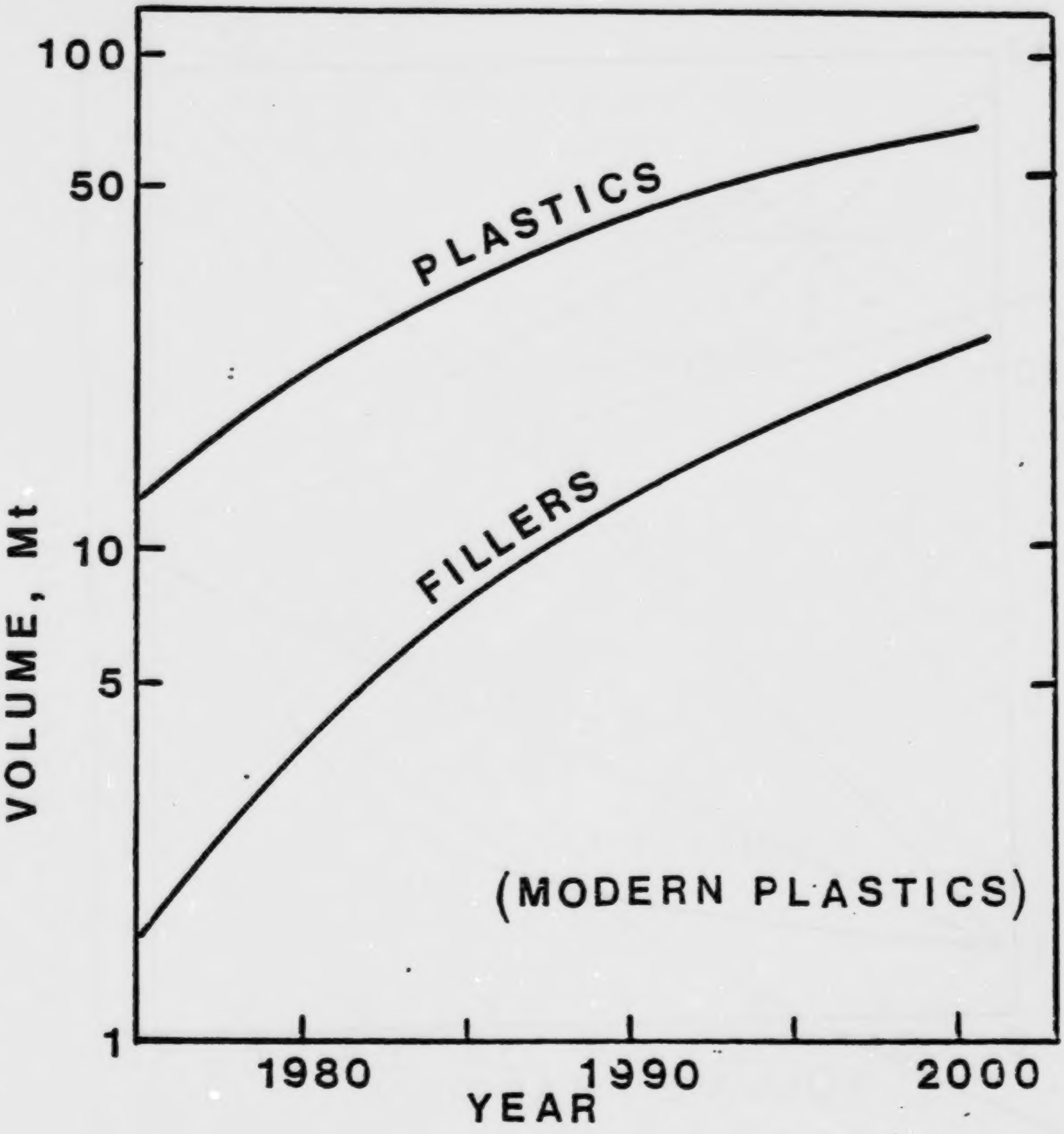

Figure 1. The predicted trend in the growth of all types of fillers parallels the growth of plastics during the next 20 years (after Reynold and Roussopoulos, 1978).

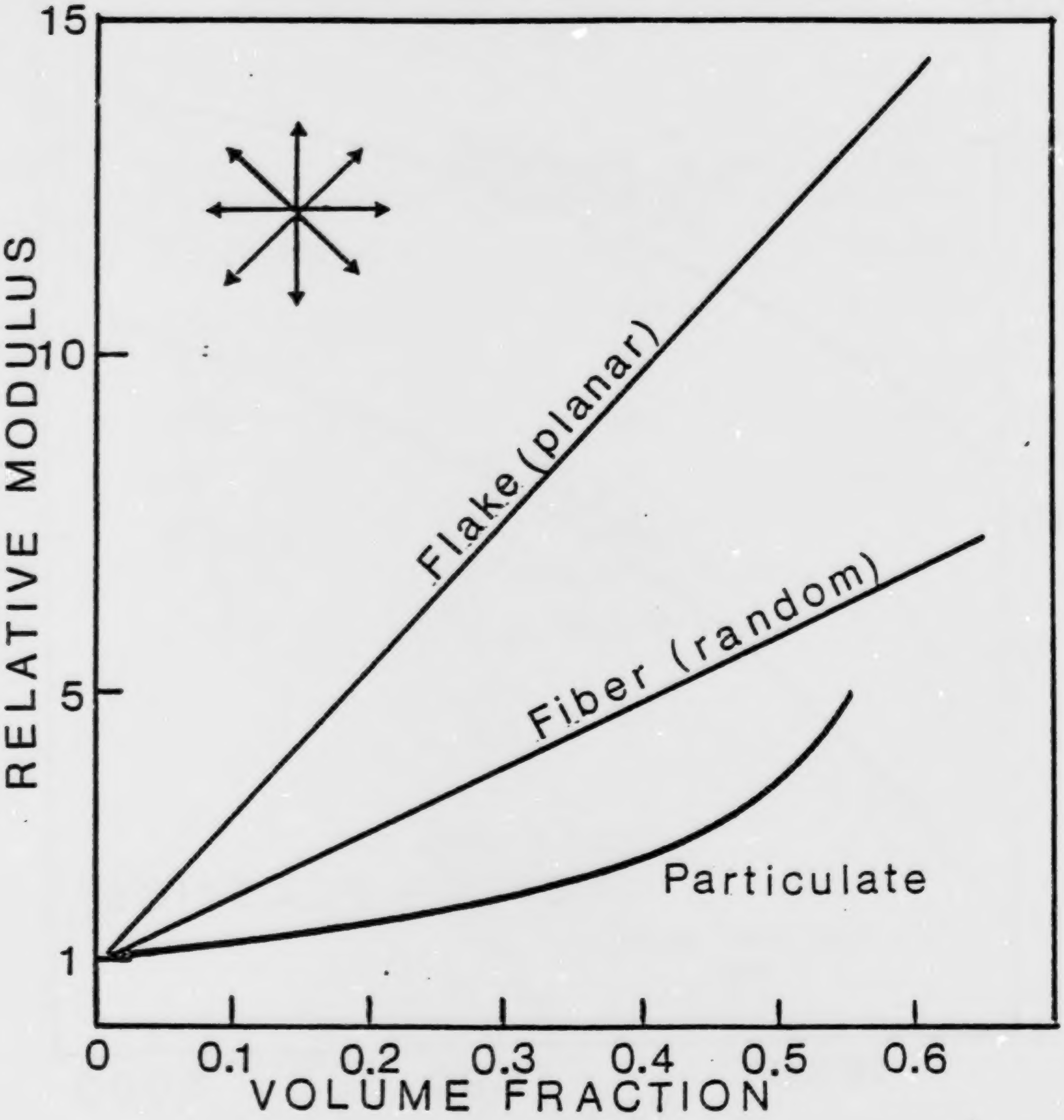

Figure 2. Glass flakes, if they were available in suitable form, would be more efficient than glass fibers for planar reinforcement. Finely ground fillers or glass beads are the least efficient for modulus enhancement.

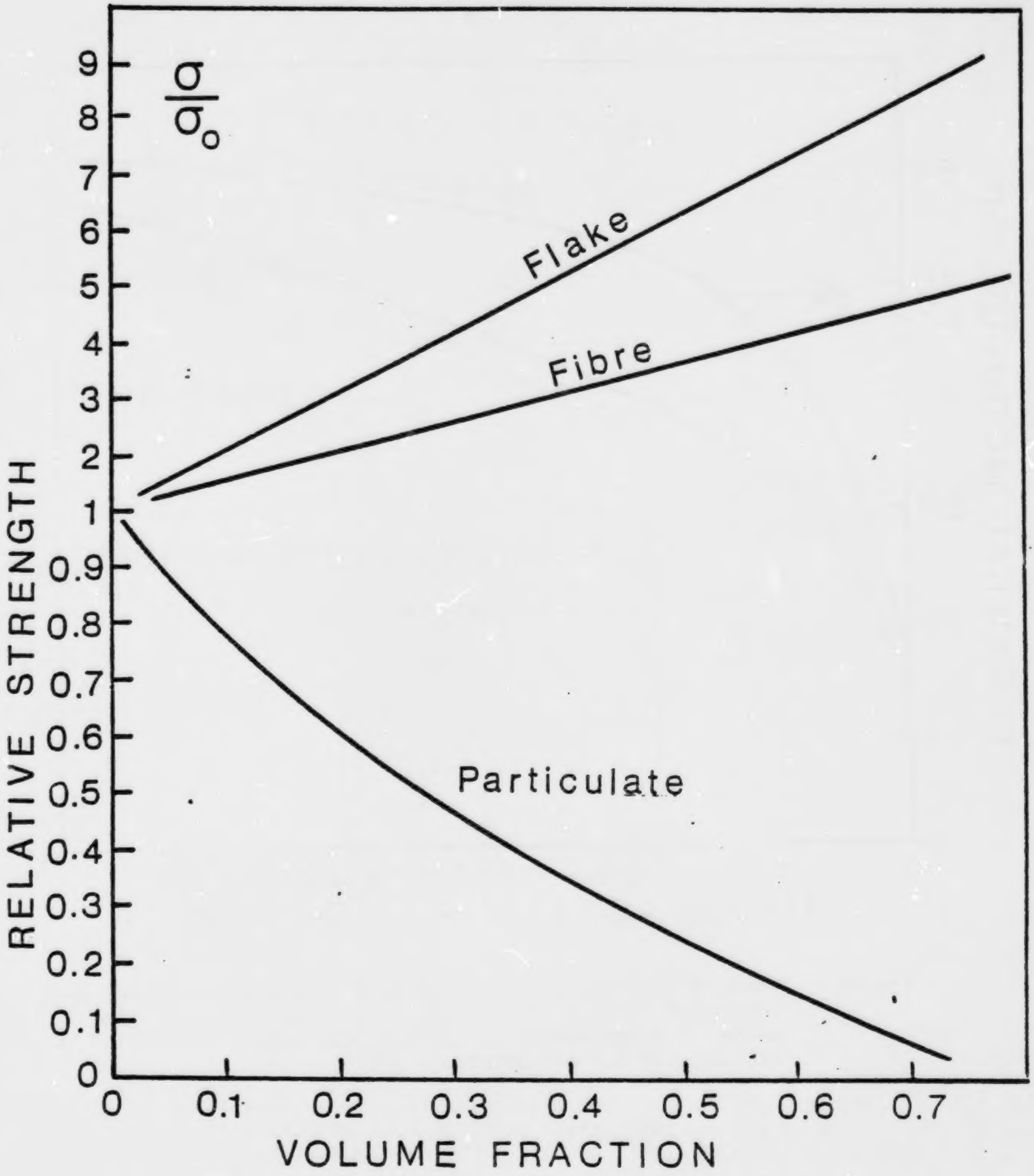

Figure 3. Most particlulate fillers tend to reduce the tensile strength or yield stress of a composite. High aspect ratio glass flakes would be more efficient than glass fibres for planar strength enhancement.

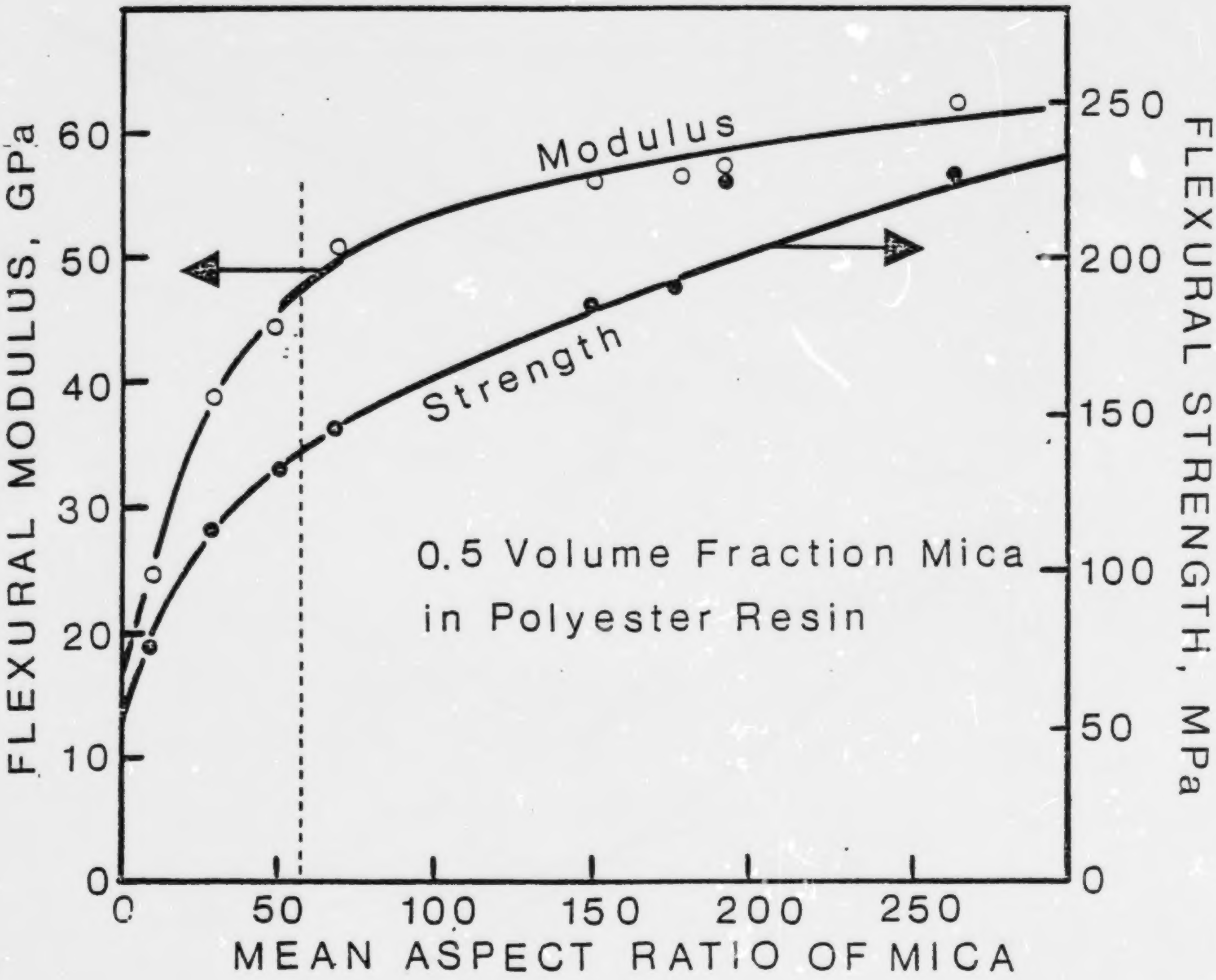

Figure 4. There is a strong dependence of both strength and modulus upon the aspect ratio of mica flakes in a polyester resin. The dashed line represents the maximum mean aspect ratio which is available in current commercial grades of mica.

SZEGO GRINDER

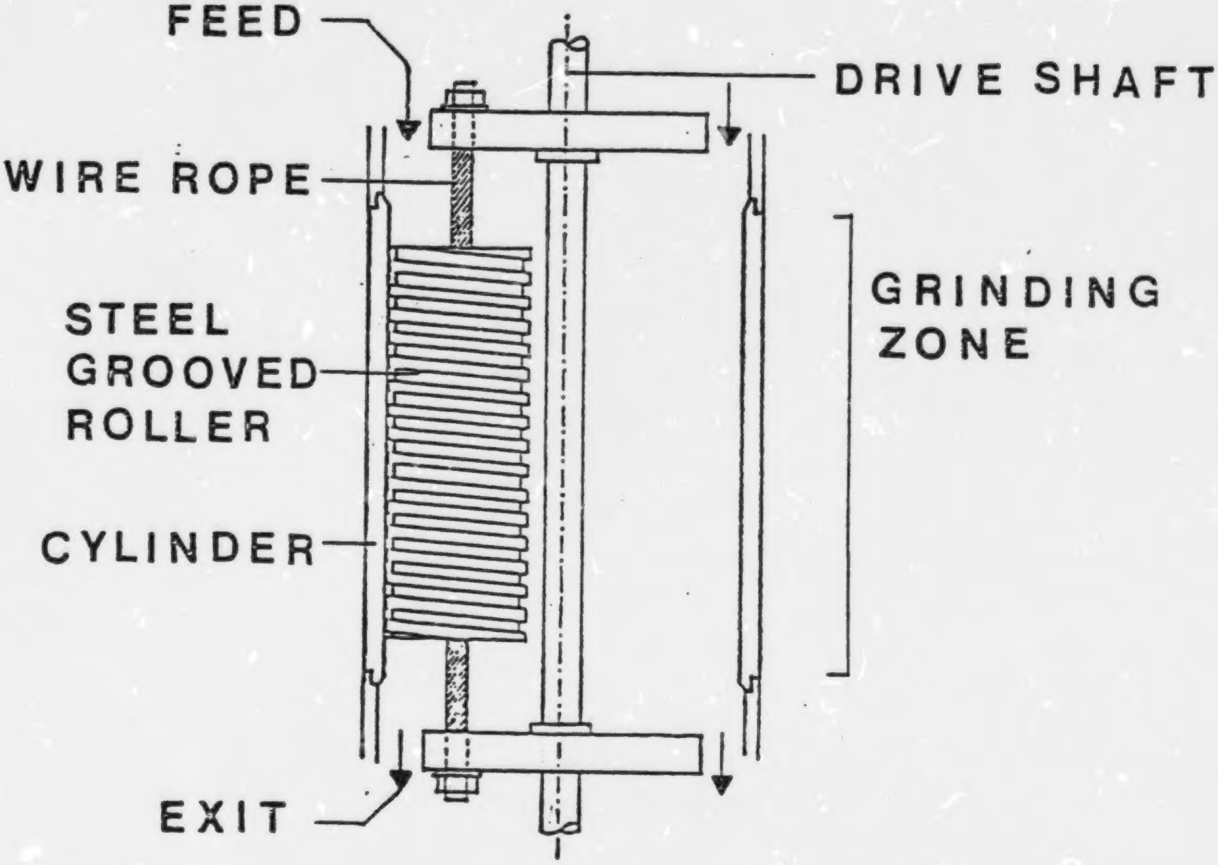
FEED
DRIVE SHAFT
WIRE ROPE
GRINDING ZONE
STEEL GROOVED ROLLER
CYLINDER
EXIT

Figure 5. A cut-away view of the Szego mill shows one of the grooved rollers attached to a rotating shaft. Various wet or dry feeds may be accommodated to produce finely ground fillers more efficiently than jet mills.

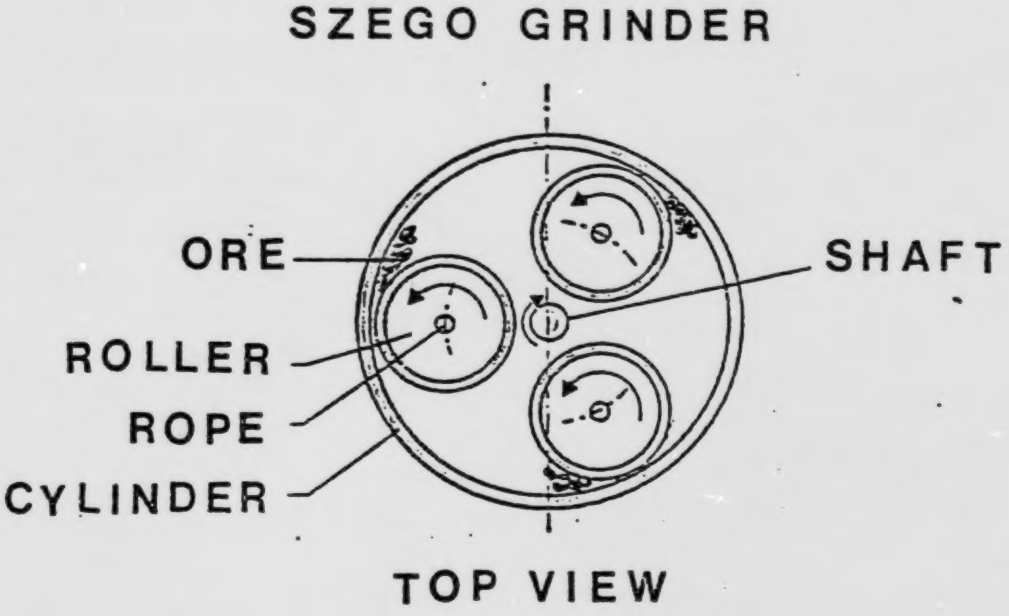
SZEGO GRINDER
ORE
SHAFT
ROLLER
ROPE
CYLINDER
TOP VIEW

Figure 6. A top view of the Szego mill illustrates the placement of the three rollers which rapidly crush the ore particles to a fine powder (as small as 5 microns).

ONTARIO RESEARCH FOUNDATION

CANMET

SYMPOSIUM

USE OF CEMENT KILN DUST AS A FILLER IN ASPHALT MIXES

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USE OF CEMENT KILN DUST AS A FILLER IN ASPHALT MIXES

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SUMMARY

While the beneficial use of fillers in asphalt mixes is generally recognized (hydrated lime for anti-stripping purposes, cement kiln dust as general filler in hot mix asphaltic concrete and pipe protective coatings, for instance), such applications are not common in Ontario. The St. Lawrence Cement Company, recognizing the potential for utilization of their by-product cement kiln dusts as a filler in asphalt mixes, initiated a materials research program at McMaster University to develop such usage. This research, and limited plant trials, have shown that cement kiln dust makes a most satisfactory filler in asphalt mixes, both as an inert addition and one that becomes somewhat active in developing beneficial properties such as a reduced temperature and oxidation susceptibility. Of greatest importance, the blending of cement kiln dust into the asphalt cement, before incorporation with the aggregate, results in a binder (mastic) that can significantly reduce asphalt cement requirements. Laboratory studies on such combined binders and their use in asphaltic concrete mixes have indicated that a 15 to 25 percent volume replacement of the asphalt cement by cement kiln dust should be possible. While this must be confirmed through equipment development and field trials, the economic impact is clear given the escalating cost of asphalt cement (currently about $200/tonne). The laboratory research is described along with the steps necessary to explore implementation of the large volume replacement of asphalt cement in asphalt mixes by cement kiln dust.

Prepared for the ORF/CANMET Symposium on Mineral Fillers, October 20 and 21, 1981, Toronto.

BACKGROUND

Cement Kiln Dust Production

During the production of clinker in kilns for portland cement manufacture, it is necessary for most plants to discard a proportion of the fine dust collected during air pollution control. Currently, most of this by-product cement kiln dust has to be disposed of so that transportation and landfilling costs are imposed on the manufacturer in addition to the loss of a potentially useful material. The reasons for discarding cement kiln dust relate to the overall process procedures, the nature of the market for portland cement, and the generally unfavourable costs of previously proposed methods for its use [1-4]. Portland cement clinker is manufactured by burning, usually in a rotary kiln, a raw-material blend (finely ground mixture of limestone, silica, alumina and iron oxide) containing oxides of calcium, silicon, aluminum and iron. The naturally occurring raw-materials used in the industry contain along with these elements, small quantities of sodium and potassium (alkalies). During burning, these elements are partly volatilized in the kiln to be captured as a component of the fine particulate material collected in the gas emission control equipment. The alkali content of this collected kiln dust is the most important characteristic determining whether the dust can be recycled in the manufacture of cement, which if of course, a prime objective of the cement industry. If the total alkali content is below approximately 1 percent, most of the dust can be returned to the process. However for higher alkali dusts, or bypass dust from suspension preheater kilns used in dry process plants, or where low-alkali clinker is being manufactured, the dust must be discarded.

Most Canadian plants use locally available raw materials which are generally relatively high in alkalies. Further, the improved heat efficiency of dry process preheater kilns is moving the cement industry towards a more extensive use of this type of process along with a return to coal firing [5]. The proximity of the U.S. market results in significant export activity that imposes a demand for low-alkali clinker (United States specifications often demand less than 0.6 percent equivalent alkalies). Taken together, these factors result in a current kiln dust disposal problem for much of the Canadian cement industry. In addition, efforts to improve the environment have lead to the development of new air emissions guidelines for the industry [6, 7]. These will result in an increase in the amount of kiln dust collected for most plants, further adding to the disposal problem unless uses are found for by-product cement kiln dusts. In this regard, it should be noted that recent studies have shown that cement kiln dusts do not contain leachable toxic constituents exceeding accepted environmental standards [8].

With the variability in raw-materials and several processes used in the cement manufacturing industry, it is difficult to estimate the annual Canadian production of cement kiln dust that must be discarded, rather than returned to the kiln. For the United States, an extensive study completed in 1974 by Southern Research Institute found [1]:

> The exhaust gases from portland cement kilns carry away an average of 12.2% of the kiln feed. To reduce particulate emissions, an average of 96% of this material is removed from the exhaust gases by dust collectors. Since the dust has an estimated value of $2 per ton, it is returned to the kiln whenever possible. Of the 16.4 million tons of dust collected annually from cement kiln exhausts, 11.9 million tons are returned to the cement-making process, and 4.5 million tons are discarded.

Based on the United States portland cement production of 87.5 million tons in 1973 [9], this is a cement kiln dust discard rate of 4.6% of portland cement production. For the Canadian portland cement industry, this discard rate (perhaps high in the Canadian context) would result in the need to dispose of about 0.50 million tonnes of cement kiln dust in Canada per year. This figure appears reasonable based on the estimated past quantities of cement kiln dust discarded by the St. Lawrence Cement Company.

Characteristics of Cement Kiln Dust

The main parameters that have been identified to characterize cement kiln dusts are summarized in Table 1 [10]. While cement kiln dust has a wide variation in these parameters from plant-to-plant, kiln-to-kiln and day-to-day, the composition data shown in Table 2 for the St. Lawrence Cement Company are probably typical. The composition variability data given in Table 3 are very important as they indicate the wide range of composition to be anticipated, and accounted for in any potential utilization. Since calcium oxide is the major component of all portland cements, kiln dusts invariably contain large amounts of lime as indicated in Tables 2 and 3. In this regard, the free lime (free CaO) is of particular interest since hydrated lime is often used to improve the stripping resistance when siliceous aggregates are used in asphalt mixes.

The potential uses for waste cement kiln dust indicated in the Southern Research Institute study include: fertilizer component; soil conditioner; potassium source; soil stabilization; neutralization of acidic wastes; absorption of SO_2 from stack gases; water treatment; glass making; production of lightweight aggregate; and filler in asphalt mixes [1]. Generally, until recently, economic factors have not favoured such uses and/or the technical background has not been adequately developed to encourage usage [1-4]. The wide spectrum of potential uses for by-product cement kiln dust, and recent progress in developing uses such as sludge stabilization and road base construction are detailed in the companion paper "Potential Uses for Kiln Dusts" and will not be discussed further here.

It would appear that the economics of using by-product cement kiln dust as a filler in asphalt mixes, particularly as a substitute for hydrated lime, are favourable since a demand for such fillers exists [11] and no processing is required for normal dust, while a simple process for emulsion precoating to expedite handling has been developed by the St. Lawrence Cement Company. Further, the by-product kiln dust is available near urban demand points for asphalt mixes so that transportation costs are minimized. Of key importance, utilization as a filler tends to involve bulk quantities, thus reducing disposal problems while substituting for more expensive fillers. Unfortunately, the technical background for the use of cement kiln dust as a filler in asphalt mixes has not been adequately developed or demonstrated. For this reason, the St. Lawrence Cement Company initiated the materials research program summarized herein at McMaster University. Since emulsion precoating of the waste cement kiln dust offers significant handling advantages at both the cement and asphalt plants, and there may also be technical advantages in asphalt mixes such as better mixing and void filling, emulsion precoated dust was initially considered in parallel to normal cement kiln dust.

FILLERS FOR ASPHALT MIXES

While a definition of filler is not universally adopted, that given by the Ontario Ministry of Transportation and Communications (MTC) is representative of most and is the operating definition for Ontario:

> 1003.06 FILLER
>
> Filler shall consist of mineral filler, hydrated lime, portland cement, asbestos fibre, or other material as designated and currently approved by the Ministry for use in asphaltic concrete.
>
> 1003.06.01 MINERAL FILLER
>
> Mineral filler shall consist of thoroughly dry limestone or other mineral dust approved by the Ministry, shall conform to the current Ministry requirements for chemical analysis and quality, and shall be consistently graded to meet the following gradation requirements.

Passing600 μm Sieve	100%
Passing 75 μm Sieve - - not less than	80%

It is clear that these specifications are neither explicit or indicative of relative filler quality. Further, both hydrated lime and portland cement fillers are too expensive for most applications, and only limited quantities of asbestos fibre are available (noting that safety precautions are critical). While cement kiln dust is not directly mentioned, there is little doubt that it meets the MTC requirements for mineral filler from the few citations in the literature, and some preliminary investigations by F.J. Pounder Limited of Brampton for the St. Lawrence Cement Company.

The ASTM definitions of mineral fillers for use in slurry seals are much more explicit in terms of the filler's role.

> 4.0 Mineral Filler
>
> 4.1 Mineral fillers are of two types, Chemically active and chemically inactive. Both shall conform to ASTM Specification D242 for Mineral Fillers for Bituminous Mixtures.

4.2 Chemically active mineral fillers such as portland cement, hydrated lime, and ammonium sulfate are used to improve the workability, regulate the setting time and, in some cases, to alter the aggregate gradation.

4.3 Chemically inactive mineral fillers such as limestone dust, flyash and rock dust are used mainly to alter aggregate gradation.

If the role of various fillers in asphalt mixes is summarized, it becomes clear that there is a ranking of fillers in terms of desired effects on the particular mix [12-16]:

1. Filler particles smaller than the thickness of asphalt films (i.e. suspended filler in asphalt cement) and asphalt cement form a mastic that is more viscous and less temperature sensitive, and in the case of hydrated lime (and perhaps portland cement), probably decreases the rate of hardening of the mastic due to a saponification reaction which results in softening of the asphalt cement.
2. Filler particles larger than the thickness of asphalt films become a void filling part of the mineral aggregate contributing to the contact points between individual aggregate particles (i.e. strength improved).
3. Hydrated lime (and perhaps portland cement) as a filler contributes to the durability of asphalt mixes containing siliceous aggregate by improving the asphalt cement-aggregate bonds. (For aggregates that are difficult to dry completely, such additions are very helpful.)
4. For slurry seals, hydrated lime and portland cement additions are often used to improve or modify workability and setting properties.

Thus, it would appear that hydrated lime is the filler that offers the most beneficial effects in addition to a void filling role, i.e. decreased rate of hardening and improved stripping resistance. This is the potential replacement market of greatest interest for both low (2% to 6%) and high (>10%) level cement kiln dust additions as filler in asphalt mixes.

CURRENT EXPERIENCE

A literature survey and industrial enquiries during the early stages of the study indicated that while cement kiln dust has not been used as a filler in asphalt mixes in Canada, it is used in Italy in asphaltic concrete for highway paving, and in the United States in special fine asphalt mixes for pipe coatings. It is probable that there are other current asphalt mix (asphaltic concrete, mastics, roofing, etc.) filler applications for cement kiln dust, but these do not seem to be documented [17].

By-product cement kiln dust has been used for several years in Italy as a filler in asphaltic concrete mixes with good results from both a technical and economic viewpoint [17]. Available information concerning the characteristics of asphaltic concrete mixes with different fillers (cement kiln dust, steel slag dust, portland cement, flyash, rock asphalt powder, hydrated lime) at a 6 percent addition rate indicates that mixes with cement kiln dust as filler compare favourably with those using hydrated lime as filler, and the flow properties are somewhat better. It would appear that cement kiln dust has established a good market value (about 30 to 50 percent of portland cement price) for use as a filler in asphalt mixes. In addition, some laboratory data for binders (mastics) of asphalt cement mixed 50/50 by weight with cement kiln dust indicates the potential for such large asphalt cement replacements, but the ductility was reduced significantly. The use of such large filler additions to make a binder is similar to natural asphalts such as Trinidadian that contains 39 percent fine solids [18]. It seems that cement kiln dust is suitable as filler in the various mastic asphalts that are popular in Europe. If more mastic asphalts are used for concrete bridge deck protection this could be a significant potential application for by-product cement kiln dust. Regardless, the possible incorporation of filler as an asphalt cement "extender" should be noted as this was studied in the laboratory work described below, and appears technically sound.

For fine asphalt mixes used in waterproof pipe coatings, about 12 percent cement kiln dust has been incorporated at some plants. The resulting mix is extruded as a covering on the pipe. Unfortunately, published data is not available on the process, but construction industry sources indicate the cement kiln dust makes an excellent filler in the process.

LABORATORY STUDIES OF CEMENT KILN DUST AS FILLER AND EXTENDER

Low Level Additions as a Conventional Filler

The initial laboratory work involved the comparison of low level additions of various fillers, including cement kiln dusts (cement kiln dust from wet kiln precipitator, bypass cement kiln dust, 10 percent emulsion content precoated cement kiln dust), in typical asphaltic concrete mixes. The various fillers involved, and their typical gradations, are indicated in Table 4 where the natural filler (baghouse dust), hydrated lime and ground limestone were included as controls. Considerable data were generated, but only the key aspects will be summarized here.

One of the first aspects considered was the technical advantages of emulsion precoating (10 percent emulsified asphalt) the cement kiln dust. While such precoating offers handling and transportation advantages, and the emulsion is largely recovered following incorporation into the asphaltic concrete mix, the process adds to the cost and no mix technical advantages were found over non-coated cement kiln dust and bypass cement kiln dust. For this reason, no further work was done on the more costly emulsion coated cement kiln dust.

Typical asphaltic concrete test results for HL3 surface course mixes with various low level filler additions are summarized in Table 5. It is clear that cement kiln dusts are suitable as fillers for use in asphaltic concrete and give comparable mix characteristics to natural filler, hydrated lime and ground limestone. Limited aging and durability studies indicated that cement kiln dusts share some of the documented advantages of hydrated lime, but as anticipated from their much lower free lime content, they are not as effective.

A fairly common use of hydrated lime in asphalt technology is as an anti-stripping addition (typically 1 percent addition) to asphaltic concrete mixes containing aggregate subject to stripping of the asphalt cement binder. This application was checked for cement kiln dusts in an asphaltic concrete mix with aggregates (siliceous) subject to stripping. The data summarized in Table 6 indicates the cement kiln dusts were not effective in this use (they did have a good visual stripping rating) when compared to hydrated lime. This lack of stripping resistance improvement is again probably related to the much lower free lime content.

Portland cement and hydrated lime are both used as low level active fillers in slurry seals (mix of fine aggregate and emulsified asphalt). To consider the use of cement kiln dusts in slurry seals, designs were carried out using cationic emulsified asphalt, stripping problem aggregate and silica sand. Abrasion resistance testing showed the following abrasion losses in gm/ft^2 for 2 percent filler addition: no filler - 29.3; ground limestone - 22.4; bypass kiln dust - 19.0, cement kiln dust - 13.9; portland cement - 12.0; and hydrated lime - mix not suitable. An abrasion loss of less than 50 gm/ft^2 is considered acceptable and the mix containing cement kiln dust gave excellent results. Cement kiln dusts appear to be most satisfactory for use in slurry seal applications. Unfortunately, this market is limited as slurry seal volumes are small.

The testing of low level additions of cement kiln dust in asphalt mixes indicates this is a technically sound application, with the exception of replacing hydrated lime where anti-stripping resistance is required. It is not clear that such use will be economically attractive given the availability and low cost of natural fillers (i.e. baghouse dust or screenings dust), except in slurry seals where portland cement is replaced. However, the low level testing indicated some potential for high level additions as an extender to the expensive asphalt cement component in asphalt mixes.

High Level Additions as an Extender

The low level additions, Italian experience, cement kiln dust use in fine asphalt mix for pipe coating, nature of natural Trinidadian asphalt and limited MTC laboratory tests on blended cement kiln dust - asphalt cement binder, indicated the potential for using cement kiln dust as an economic extender for asphalt cement that is becoming increasingly expensive. Such extension is now the norm using sulphur, but the economic advantages are clearer with much cheaper cement kiln dust.

Preliminary mixing trials indicated that the filler should be thoroughly premixed into the asphalt cement to give a mastic and then kept in suspension to ensure a uniform binder and to avoid coating the asphaltic concrete aggregate with dust. The next stage involed the characterization of the fillers in Table 7 for binders with various filler - asphalt cement blends. These penetration, softening point and kinematic viscosity tests are summarized in Table 8. With the exception of the much coarser and heavier iron oxide which tended to separate out readily, no problems were encountered in preparing and testing the various filler - asphalt cement binders. While some stiffening is indicated for the blended binders in Table 8 (i.e lower penetration, higher softening point, higher kinematic viscosity), the degree was much less than anticipated. Economics would tend to rule out the use of slag cement as an extension filler (see right column of Table 8) and the mixing and separation problems with iron use make its use as an extension filler problematic. Both cement kiln dust and flyash use as an extension filler (15 to 25 percent volume replacement) appear technically feasible and economically attractive. Of course, ductility and durability testing of the blended binders would be required before implementation.

Given the favourable binder characterization results, particularly with the cement kiln dust and flyash - asphalt cement blends, Marshall testing was completed using these blends as binders in HL3 surface course asphaltic concrete mixes as summarized in Table 9. These results appear most favourable as the Marshall design values compare with those of the control with no filler addition, and in the case of the higher volume percent cement kiln dust - asphalt cement binder, all of the specifications are clearly satisfied. Again, it must be emphasized that further testing such as flexural fatigue and durability must be completed before implementation. Given the positive influence of free lime on durability, this may not be a concern with cement kiln dust.

IMPLEMENTATION

The laboratory studies, coupled with economic considerations, indicate that in addition to conventional low level filler use in asphalt mixes, cement kiln dust, and likely flyash with more mix design work, can probably be used to replace 15 to 25 percent of the asphalt cement on a volumetric basis in asphaltic concrete mixes. This is of course subject to completion of further performance checks on aspects such as fatigue resistance and durability. Following completion of further testing, implementation would involve the design of appropriate blending facilities and mixing equipment to keep the filler suspended in the extended binder. These are fairly standard techniques in the roofing and waterproofing asphalt business and should be readily developed at the refinery or hot mix asphalt plant. It may even be possible to design a direct volumetric blender on the asphalt cement feed to the hot mix asphalt plant as is done with some sulphur extended asphalt processes. The ultimate key to implementation would then be a series of trial sections to demonstrate the cement kiln dust - asphalt cement binder technology in order to receive specification approval.

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TABLE 1

CEMENT KILN DUST CHARACTERIZATION PARAMETERS

Chemical	CO_2 K_2O SO_3 $C\ell$
Mineralogical	carbonate $KC\ell$ $(K,Na)_2SO_4$ CaO_{free} (incl. $Ca(OH)_2$)
Particle size	% retained on 11 microns % retained on 39 microns
Production information	type of production system dust production rate

TABLE 2

TYPICAL CEMENT KILN DUST ANALYSES

Yearly Average	Bypass Precipitator Dust (Dry Process) %	Wet Kiln Precipitator Dust (Wet Process) %
Loss on Ignition	18.1	24.5
SiO_2	11.3	14.2
Al_2O_3	3.3	4.1
Fe_2O_3	1.5	1.5
CaO	34.1	44.0
MgO	1.4	1.8
Cl	7.3	2.0
SO_3	7.0	3.1
K_2O	16.5	6.3
Free CaO (Individual Samples)	12.0 12.5 9.1	2.5 2.9 2.4
K_2O (Weekly Range)	9-27	4-15
Cl (Weekly Range)	4-28	0.5-5
SO_3 (Weekly Range)	3-13	3-13

TABLE 3

TYPICAL COMPOSITION VARIABILITY OF CEMENT KILN DUST BY KILN TYPE AND PRECIPITATOR SOURCE

(18 Month Sampling Period)

A. Bypass Precipitator (Dry Process)

	$C\ell$	SO_3	K_2O	Free CaO
n[a]	58	58	58	14
$\bar{x}$	14.21	6.70	20.15	6.77
σ	7.95	2.48	5.98	2.99

B. Total Wet Kiln Precipitators

	$C\ell$	SO_3	K_2O
n	68	68	68
$\bar{x}$	1.45	4.76	5.77
σ	0.64	1.16	1.43

C. Last Three Cells Wet Kiln Precipitators

	$C\ell$	SO_3	K_2O	Free CaO
n	61	61	61	35
$\bar{x}$	2.63	7.56	9.95	1.63
σ	1.41	3.00	3.09	0.98

NOTE

a. n = number of samples, $\bar{x}$ = mean, and σ = standard deviation

TABLE 4

TYPICAL GRADATIONS OF FILLER MATERIALS
PERCENT PASSING

Filler	150 µm	90 µm	45 µm	30 µm	10 µm
Natural (baghouse dust)	74	65	57	45	26
Cement Kiln Dust	99	90	65	32	8
Bypass Cement Kiln Dust	99	99	94	65	4
Emulsion Coated Cement Kiln Dust	99	72	55	43	5
Hydrated Lime	99	95	87	73	50
Ground Limestone	99	97	94	89	26

TABLE 5

MARSHALL TEST RESULTS FOR HL3 SURFACE COURSE ASPHALTIC CONCRETE MIXES WITH VARIOUS FILLER ADDITIONS

(5.5% Asphalt Cement Content, Passing 75 μm
kept Constant at 4% by Volume)

Filler Added[a]		Voids Mineral Aggregate %[b]	Air Voids %	Flow 0.25 mm	Stability kN
Specification[c]		15 minimum	2 to 4	9 minimum at 2% air voids	7.00
Natural		16.1	3.4	11.7	11.44
Cement kiln dust Natural	1% 3%	16.6	3.9	11.4	11.26
Cement kiln dust Natural	3% 1%	16.5	3.7	12.4	12.06
Bypass cement kiln dust Natural	1% 3%	15.8	2.9	12.4	12.15
Bypass cement kiln dust Natural	3% 1%	15.4	2.6	12.4	11.66
Hydrated lime Natural	1% 3%	16.4	4.0	11.9	11.75
Hydrated lime Natural	3% 1%	15.4	2.6	12.2	12.59
Ground limestone Natural	1% 3%	17.2	4.5[d]	10.6	11.71
Ground limestone Natural	3% 1%	17.8	5.1[d]	11.5	11.09

NOTES

a. Filler added refers to minus 75 μm material. Constant 4% by volume maintained.
b. VMA of test specimens not corrected for absorbed asphalt cement.
c. MTC Form 310 specification. (These specifications changed in August, 1981).
d. Out of specification

TABLE 6

IMMERSION MARSHALL TEST RESULTS (MTC) FOR HL4 ASPHALTIC CONCRETE MIX FOR AGGREGATES SUBJECT TO STRIPPING

(5.5% Asphalt Cement Content, 64% Quartzite Stone, 34% Silica Sand, 2% Filler)

Filler Type	Filler Proportion of Total Aggregate %[a]	Non-Immersed Stability kN	24 Hour 60^{0}C Immersed Stability kN	Retained Stability %[b]	Visual Stripping Rating[c]
Natural (quartzite dust)	2	20.30	10.02	49	9
Natural Bypass cement kiln dust	1 1	18.70	8.43	45	7
Natural Cement kiln dust	1 1	20.07	9.96	50	7
Natural Hydrated lime	1 1	20.71	16.67	80	6
Natural Ground limestone	1 1	18.44	12.54	68	9

NOTES

a. In all cases the percentage of aggregate and filler passing 75 µm was 3.3.
   All filler quantities adjusted so that volume percentage added was the same in each case.
b. MTC procedure. The higher the percentage the better.
c. MTC procedure. The lower the number the better.

TABLE 7

GENERAL FILLER CHARACTERISTICS

Filler	Blaine Fineness cm^2/g	Specific Gravity
Cement Kiln Dust	4925	2.75
Iron Oxide	897	3.45
Flyash	3773	2.46
Slag Cement	3925	2.86

TABLE 8

PENETRATION, SOFTENING POINT AND KINEMATIC VISCOSITY TEST RESULTS FOR BINDERS VARIOUS FILLER-ASPHALT CEMENT BLENDS

Filler	Volume Percent of Filler	Penetration at 25°C	Softening Point °C	Kinematic Viscosity at 135°C centistoke	Approximate Cost for Equivalent Volume $/tonne[a]
Control (Asphalt Cement)	0	58	47	472	200
Cement Kiln Dust	10	38	54	569	182
	20	31	56	780	163
	30	27	58	1234	145
Iron Oxide	10	46	65	649	182
	20	31	70	1037	164
	30	22	75	not able to determine	146
Flyash	10	42	53	537	181
	20	35	55	740	163
	30	25	60	1308	144
Slag Cement	10	36	54	571	196
	20	29	56	671	191
	30	21	65	881	187

NOTE

a. Based on: cement kiln dust, iron oxide and flyash at $6.00/tonne; slag cement at $55.00/tonne; and asphalt cement at $200.00/tonne.

TABLE 9

MARSHALL TEST RESULTS FOR HL3 SURFACE COURSE ASPHALTIC CONCRETE MIXES INCORPORATING VARIOUS PREMIXED FILLER-ASPHALT CEMENT BLENDS AS BINDER

(Binder Volume Kept Constant at Equivalent to 6.5% Asphalt Cement Content)

Filler	Volume Percent of Filler	Bulk Density kg/m³	Voids Mineral Aggregate %[a]	Air Voids %	Flow 0.25 mm	Stability kN
Specification[b]	0 (i.e. 6.5% AC)	---	15 minimum	2 to 4	9 minimum at 2% air voids	7.00
Control	0 (i.e. 6.5% AC)	2365	19.3	3.9	13.6	11.66
Cement Kiln Dust	10	2397	20.3	4.7[c]	14.4	13.17
	20	2393	18.7	3.1	15.1	13.93
	30	2365	17.8	2.5	13.5	14.18
Iron Oxide	10	2370	22.1	6.7[c]	12.2	12.88
	20	2394	21.9	6.5[c]	11.5	13.37
	30	2389	23.6	8.1[c]	12.3	15.40
Flyash	10	2377	20.2	4.9[c]	11.4	12.75
	20	2373	20.9	5.8[c]	12.1	12.84
	30	2377	21.1	6.1[c]	13.5	15.46
Slag Cement	10	2370	21.2	5.8[c]	11.6	11.94
	20	2393	22.0	6.4[c]	12.3	14.01
	30	2410	21.2	5.5[c]	13.8	15.40

NOTES

a. VMA of test specimens not corrected for absorbed asphalt cement.
b. MTC Form 310 specification (these specifications changed in August, 1981).
c. Out of specification.

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SYMPOSIUM

MINERAL FILLERS IN ASPHALTS

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TREMCO

MINERAL FILLERS IN ASPHALTS

By: Ken McCallum

A) Asphalt:

The definition of asphalt as given in the "Chemical Dictionary" is as follows:

"A dark-brown to black cementitious material, solid or semi-solid in consistency, in which the predominating constituents are bitumens which occur in nature as such or are obtained as residue in petroleum refining. It is a mixture of paraffinic and aromatic hydrocarbons and heterocyclic compounds containing sulphur, nitrogen and oxygen."

Asphalts are classified by a number of methods. Most commonly used is the penetration technique. The value given is the depth in tenths of a millimeter that a needle of specified mass and shape will penetrate in a 5 second period. As a general guide, any asphalt having a penetration of less than 25 is considered hard, 25-100 medium, and 100 or greater is soft. They are also classified as to origin, for example, California, Pennsylvania, Trinidad, etc., or by treatment. One common treatment is known as blowing. Blown asphalts are black, friable solids. They are obtained by blowing air at high temperature through petroleum derived asphalts. This produces a non-Newtonian fluid, ideal in its rheological properties for roofing. Weather resistance of the asphalt is improved. Penetration values are 10-40; softening point is between 85-100°C. (185-250°F.) Other names are condensed asphalt, oxidized asphalt or "Hard Hydrocarbon". Uses are primarily roofing, and as diluent in low grade rubber products.

Further common treatments for asphalt are solvation in suitable petroluem distillates usually referred to as "asphalt-cutbacks"

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or emulsification. Both types of asphalt treatment are used for products where a cold application if desirable. Furthermore, solvents aid wetting or penetration of the substrata.

Asphalts are used for a large number of applications and in many diverse industries. To name a few: paving and road coating, roofing, sealing and joint filling, specialty paints, diluent in low grade rubber products, medium for radioactive waste disposal, pipeline and underground cable coatings, rust preventive hot dip coatings, base for synthetic turf, water retaining barrier for sandy soils, etc. I am sure, we could find many more interesting uses.

Properties of Asphalt:

Asphalts are widely used because of their many useful chemical and physical properties. In addition, valuable features are their low cost and well established history of use.

Historically, asphalts have been low priced by-products of the petroluem industry. With rising petroleum prices and reductions in supply, the oil companies are now upgrading asphalts into higher priced materials. Hence, prices are rising and supplies are declining.

Asphalts have good to excellent water resistance which makes them a popular base for waterproofing applications.

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Asphalts are reasonably resistant to photo-degradation which makes them suitable for exterior applications, i.e., paving and roofing. They do, however, contain a certain degree of unsaturation which does limit exterior durability. Chemicals may be added to slow down the aging process, but it is generally found that fillers do an adequate job while improving other properties at the same time. Within certain temperature limits, asphalts have reasonably high but not outstanding physical strength, both in tensile and compression. Since strength is limited, reinforcement is required for maximum durability.

Asphalts are thermoplastic, that is they soften and melt at elevated temperatures. This characteristic allows for easy processing and application such as required for hot paving and roofing. The same thermoplastic properties cause asphalts to have flow stability, or sag resistance problems. The reason for this behaviour is that asphalts are not pure chemicals, hence, they do not exhibit clearly defined melting points. Before transition from solid to liquid occurs, there is a wide range of temperatures where asphalts are extremely viscous substances. Control of the latter rheological properties requires modification, and causes the chemist many a headache.

Asphalts tend to be brittle at low temperatures. Since this is a serious handicap, modification by many means is often required. Generally, these modifications require addition of plasticizers, rubbers and fillers.

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B) Fillers:

The Chemical Dictionary defines filler as "an inert mineral powder of rather high specific gravity (2.00 - 4.50) used for example, in asphalt compounds, plastic compounds and rubber mixtures to provide a certain degree of stiffness and hardness and to decrease cost. Examples are calcium carbonate (whiting) barytes, blanc fixe, slate flour, soft clays, talcs, etc. Fillers have neither reinforcing nor colouring properties and the term should not be applied to materials that do, i.e., reinforcing agents or pigments. Fillers are similar to extenders and diluents in their cost reducing function.

Depending on the use of the end product, fillers generally should be non-hygroscopic since water absorption often degrades properties. Chemical resistance is also desirable in many situations. Ideally, fillers for asphalts should be opaque, if the product is used for exterior exposure. This tends to reduce photo-oxidation of asphalts and thus improves exterior durability.

General Classification of Fillers

Mineral fillers used in asphalt products can be classified in three major groups based on their physical shapes, such as fibers, plates and granulas.

Fibres

Without question, the most common fibrous filler is asbestos.

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It finds extensive use in roofing and sealing and joint filling compounds . Unfortunately, asbestos has been under heavy attack and industry is working desperately for a substitute. To my knowledge, no replacement having the universal properties of asbestos has been found.

Plates

Fillers which resemble microscopically flat sheets or platelets include the clays and are typified by ground mica.

Granulas

The largest group being neither fibre nor plate consists of compounds with a regular crystalline structure or shape. Here we find ground limestone, ground marble, ground silica, talcs, barium sulphates, nepheline syenite, powdered slags, etc.

C) Why Are Fillers Required?

Fire Resistance

Asphalts consist mostly of hydrocarbons which means that they will burn when exposed to open flames and high heat (auto ignition temperature 900°F). This presents a serious problem, if the asphaltic product is to be used in buildings or other places where fire hazard is a major concern.

Mineral fillers do not burn. Hence, replacement of a portion of the asphalt with mineral filler will improve fire resistance.

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Traditionally, asbestos has been the favourite filler to impart fire resistance for two reasons. The first being its reputation as a fireproof material of moderate cost. The second and often most important reason is that it will reduce the flow of the melted asphalt and thus slowing the spread of the fire.

Additional fire protection from mineral fillers can be obtained by way of physical or chemical change on heating. One example is the release of moisture resulting in intumescence or puffing.

For fire resistance, almost any mineral filler which dilutes the asphalt will do. Preferred, however, are asbestos and calcium carbonate.

Moisture Permeability

The correct choice of filler can reduce the water permeability of a product by a considerable amount. Some examples being:

- Decrease in water permeability and an increase in water absorption by the addition of 20% slate flour to air blown asphalt.
- The addition of soapstone talc to air blown asphalt has been reported to reduce the permeability of both water and oxygen.

At the same time, water absorption by immersion for one month was increased by a factor of nine. Such examples are very common in many asphalt studies. The contribution of water absorption by fillers is finite and in proportion to the asphalt/filler ratio, and the relative affinity for water of the filler.

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Exterior Durability

As stated earlier, opaque fillers contribute to partially shield the asphalt from the effects of photo-oxidation, thus increasing the work life of the material applied or used outside. Translucent fillers, such as quartz, are not as effective for this purpose.

Rheological (Flow) Properties

Because asphalts are mixtures of loosely held molecules, they tend to cold-flow. To prevent this phenomenon, a number of fillers can be added. Asbestos, clays, calcium carbonate, to name a few, may be added for this purpose. For high temperatures or solvated systems, thixotropy (shear thinning) is desirable. This allows for easy, controlled application by brush or trowel without later flow, runs or sag. Fibres, i.e., asbestos or plates such as clays (structured particles) are very useful for this purpose.

Impact Resistance and Strength

Asphalt by itself tends to be very brittle at low temperatures. The general rule is that fibres such as asbestos give the largest improvement in impact resistance while plates (clays) give the next best, and non-structured powders give the least improvement. The same trend is noted for strength. It has been known for a long time that small amounts (1-2%) of asbestos in pavement add considerably to strength. This is a factor of importance for highway pavements exposed to high wheel loads. Increased

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strength adds much to the service life of many products where thermal shock and movement will cause severe cracking or fatiguing. Anything which will increase both hardness and strength simultaneously will improve the impact strength. Many surfaces such as floors often experience impact from dropped equipment, rough placement of goods and vibrating equipment. Therefore, careful selection of fillers is necessary to ensure long service life.

Application of Mineral Filled Asphalts

Mineral filled asphalts find numerous applications, for example, Bituminous Grout, Bituminous Coatings for acid proofing of concrete surfaces, Pipe Coatings, Floor Tiles, Potting Compounds for electrical insulation, Roofing Shingles, Roofing, Highway Pavement and Pond or Lagoon Liners.

Bituminous Grout

Bituminous Grout is used as a protective coating, for membrane waterproofing, filling of joints and as a bedding compound for bricks. This material is manufactured and applied hot. Bituminous Grout is used in place of other grouts when fast set, high impermeability to water and chemical inertness are required.

A standard formulation used is:

Asphalt	45 parts by weight
Mineral Aggregate	55 parts by weight (100% pass 20 mesh screen 5% pass 200 mesh screen)

cont'd...

AIRFIELD RUNWAY PAVEMENT FORMULATION

SIEVE SIZE	PERCENT PASSING
3/4	100
1/2	91.5
NUMBER 4	85
8	57
30	23
50	19
100	11
200	6

ASPHALT: 85 - 100 PEN. 6% OF DRY AGGREGATE

AGGREGATE: GRAVEL/SAND TO MEET THE ABOVE SPECIFICATION.

The asphalt chosen will depend on the degree of hardness and the softening or melt temperature required.

Asphalt Flooring Tiles

Asphalt Flooring Tiles are not as prevelant now as in the past. Still, these tiles which have been made since 1922 find many uses.

A typical formulation would have the following composition.

Asphalt "hard"	25%
Asbestos	35%
Limestone Dust	35%
Coloured Pigment	5%

It may be noted that by replacing the hard asphalt with a softer type and replacing the coloured pigment with solvent, one can produce a simple caulking compound.

Aircraft Runway Pavement

When individuals think of uses for asphalt, the first thing most often mentioned is asphalt pavement. For this reason, I am giving a classical formulation used for paving of the runway at Fanning Field in Idaho. This particular pavement was designed to meet the landing requirements of Boeing 727 aircraft (172.000 pound dual gear loading).

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Asphalt Paved Lagoons or Ponds

Impermeability and chemical inertness allows asphalt products to find use as liners for waste treatment plants such as the one at Pfizer Chemical Co., in Southport, North Carolina.

The lagoons are lined with multiple layers consisting of:

cont'd....

ASPHALT PAVING FOR LAGOONS & PONDS

(PFIZER CHEMICAL CO., SOUTHPORT, NORTH CAROLINA)

30 MILS PVC-SHEET

12" CLAY SAND

6" CRUSHED STONE

2 LAYERS OF ASPHALT PAVEMENT

1 TOPCOAT OF ASPHALT SEALER

THE FORMULA FOR ASPHALT PAVEMENT WAS:

SIEVE SIZE	PERCENT PASSING
3/4	100
1/2	97.5
NUMBER 4	70
8	52.5
30	33
100	20.5
200	11.5

ASPHALT: 7.5 % OF DRY AGGREGATE

AGGREGATE: GRAVEL/SAND TO MEET THE ABOVE SPECIFICATION.

Note: This formulation is very similar to that of the airfield runway but it contains slightly smaller particles for better sealing.

Roofing

Today, the majority of roofs in Canada and the United States are waterproofed by asphaltic materials, either as highly filled asphaltic shingles or built-up multi ply roofing.

Most industrial, institutional and highrise buildings have flat roofs made of multiple layers of asphalt and roofing felts. Such roof membranes may be hot or cold applied and generally require a wide variety of mineral filled asphaltic materials for proper maintenance.

Hot Applied Roofing

Most hot applied roofing is composed of virtually pure asphalt although a growing number of these roofs are using modified asphalt materials. One common approach is the use of elastomer modified asphalt membrane or so-called rubberized asphalt. It overcomes the problems of brittleness, and as a result, it can accommodate movement due to thermal expansion and contraction.

An example of such formulation is:

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HOT APPLIED ROOFING

(RUBBERIZED ASPHALT)

ASPHALT	30%
RUBBER	10%
PROCESS OIL	10%
FILLER	50%

The filler normally used would be a granular type, i.e., marble dust or calcium carbonate. Fibrous fillers may be added, if increased strength is desired.

Cold Applied Roofing

Cold applied roofing is manufactured with either emulsified or solvent reduced (cutback) asphalts. Emulsified asphaltic roofing products are commercially available, and their future growth in the marketplace is anticipated. Positive characteristics of emulsified products are: no organic solvents, environmentally clean, and no fire hazard. Their use is somewhat limited due to our Canadian climate since applications are restricted to temperatures above 5°C.

Solvent reduced asphaltic roofing is composed as follows:

COLD APPLIED ROOFING

ASPHALT	45%
SOLVENT	10%
PROCESS OIL	10%
ASBESTOS	15%
CALCIUM CARBONATE	20%

ROOF ADHESIVE

HIGH SOLIDS

VERY THIXOTROPIC

This formulation produces a very thixotropic, high solids roof adhesive or mastic. For greater strength or improved non-sag properties, more asbestos may be used in place of calcium carbonate. The solvent portion may be increased depending on end use, application equipment, etc.

Other Roofing Products

Another common application for filled asphalts is their use as Roof Resaturants to revitalize aged roof membranes. Generally, asphalt becomes brittle and felts dry out due to prolonged weathering. This is where the concept of re-impregnation or resaturation offers a practical solution.

Resaturants are composed mostly of light asphalts, special oils, wetting agents and solvents, thus these binders are of very low viscosity. In order to provide thixotropy, and to balance penetration, run-off and to control application rates, up to 20% asbestos is usually added. Small amounts of up to 10% of other fillers may be added. This extra filler adds viscosity and often serves to shield the asphalt from photo-oxidation.

Waterproofing and Dampproofing

Excellent opportunities for mineral fillers exist in the field of waterproofing and dampproofing. Again, we find a great variety of asphaltic based membranes containing in addition to asphalts, elastomers and mineral fillers. The mineral filler must not: increase water permeability and water

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absorption. Depending on end use, fillers may be required to be chemically inert and they may have to contribute to control viscosity and sag resistance.

The Future of Mineral Fillers in Asphalts

The continuously rising prices of crude oil and finished petrochemicals has caused the refineries to alter their approach with respect to asphalts.

Upgrading plants are now being built to convert asphalt and other heavy refinery tailings into higher value petrochemicals, such as gasoline and plastics.

The asphalt compounding industry must now find methods of extending asphalt supplies as no inexpensive substitutes are available. Asphalt compounds of the future will be using more mineral fillers to counter increasing prices and shrinking supplies.

Fire hazard regulations are becoming more prevalent and again mineral fillers are often the cheapest and safest method of reducing combustibility.

As a result, the mineral extraction and processing industries can expect both continued technical challenges and sales growth from the asphalt compounding industries.

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POTENTIAL USES FOR KILN DUSTS

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POTENTIAL USES FOR KILN DUSTS

J. Emery
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SUMMARY

The range of current and potential applications for lime kiln dusts and cement kiln dusts is reviewed - recycling, fertilizer, chemical source, soil conditioning, neutralization of wastes, aggregate and masonry manufacture, waste stabilization, filler in asphalt mixes, binder component in base stabilization, etc. - with particular emphasis on stabilization applications. For kiln dusts that cannot be recycled for various reasons, applications in binders appear to be advantageous as the technology is developed, there are substantial materials and energy conservation benefits, and there is a fair financial return to the producer. Procedures for stabilizing sludges and sediments using kiln dusts are outlined to introduce their growing application and the technology involved. Past and current research on kiln dust-fly ash pozzolanic binders for base stabilization in highway construction are described to indicate the growing potential for this construction technique. Most of the other applications (fillers in asphalt mixes covered in a companion paper) require further technical work to develop regular utilization.

Prepared for the ORF/CANMET Symposium on Mineral Fillers, October 20 and 21, 1981, Toronto.

BACKGROUND

The solid wastes generated during cement and lime manufacture are primarily cement kiln dusts and lime kiln dusts, respectively. Details on the production of cement kiln dusts, their characteristics, and utilization as a filler in asphalt mixes are given in the companion paper "Use of Cement Kiln Dust as a Filler in Asphalt Mixes", and will not be repeated here. Lime kiln dusts are similar in many regards, and contain a mixture of raw kiln feed, partly calcined material and finely divided particles. There is generally no value in returning the dust to the kiln, as it is too fine and tends to pass directly through to the precipitators again. Up to about 15% of the raw materials processed during lime manufacture may be collected as dust which must be disposed of unless applications are available within economic transportation distance. No industry data are available, but it is estimated that there are about 0.15 million tonnes of lime kiln dust produced in Canada each year.

Typical ranges of chemistries for cement and kiln dusts are given in Table 1. Lime kiln dusts seem to have less variability than cement kiln dusts, and the limited parameters CaO, MgO, S, CO_2, loss on ignition and available lime are generally adequate for characterization. Waste quick lime kiln dusts (i.e., high available free lime) are of particular interest as they are effective in replacing hydrated lime in several conventional applications such as waste stabilization and pavement construction.

CURRENT AND POTENTIAL USES

There is a wide range of current and potential uses for cement kiln dusts and/or lime kiln dusts that must be disposed of, rather than recycled [1-6]. Recycling should of course be a prime objective given the substantial materials and energy savings potential to the manufacturer, but as indicated for lime kiln dust above and cement kiln dusts in the companion paper, there are various production and technical restrictions on the amount of kiln dust recycled. For the kiln dusts that cannot be recycled, the 'best market' in terms of financial return to the manufacturer would be those involving replacement of hydrated lime and/or portland cement, typically in cementitious and asphaltic binder systems.

One of the most comprehensive reviews of applications for cement kiln dusts has been completed by Davis [4-6], and many of the uses are applicable to lime kiln dusts. Of the wide range of potential uses for cement kiln dust and/or lime kiln dust - fertilizer component, soil conditioner, potassium source, chemical source through leaching and dust return, neutralization of acidic wastes, absorption of SO_2 from stack gases, glass making, production of lightweight aggregate, binder component in autoclaved masonry, waste stabilization, soil stabilization, kiln dust-fly ash binders, filler in asphalt mixes, etc., - this paper focuses on the stabilization potential for waste treatment and highway construction. Stabilization applications (and filler applications covered in the companion paper) offer the advantages of available technology, large volume usage, and good financial return due to replacement of conventional binder components. It would appear that significant technical effort is required to get most of the other applications to the demonstration and usage stage. For instance, in spite of numerous suggestions to market cement kiln dusts as a potassium-lime fertilizer, only a few cases are known where this has been done successfully.

SLUDGE AND SEDIMENT STABILIZATION

There is wide scope for the use of kiln dusts in the stabilization of liquid wastes, sludges and sediments to meet environmental and engineering requirements. The stabilization process developed for a high water content sludge and sediment mixture, removed during the reclamation of an old harbour area, will be described to introduce the concepts involved [7]. Other applications for the process have been developed including solidification of very soft sediments and basic oxygen furnace clarifier sludge. Waste stabilization applications for byproduct kiln dusts (waste plus waste technology) are economic and offer significant materials and energy conservation potential as primary lime and cement components are replaced.

The general stabilization process involves a number of possible combinations and proportions of sludge/sediment with stabilizing agents - fly ash, cement kiln dusts, lime kiln dusts, steel slag fines, portland cement and slag cement - to give various strengths for the highly variable sludge/sediment. A wide range of kiln dusts have been used, with low level or no cement addition, to minimize costs and to ensure stabilization materials supply continuity. Construction soil stabilization methods have been adopted involving initial drying by high surface area materials (fly ash, kiln dust) and then pozzolanic and/or hydraulic reactions as required. For disposal to landfill, just some drying and fairly low strength (shear strength ≈0.01 to 0.02 MPa) is required. The reader interested in a more complete review of stabilization technology than can be incorporated here will find the volumes edited by Pojasek [8] most helpful, including the use of kiln dusts to treat acid wastes.

Laboratory Stabilization Trials

The sludge/sediment involved was fairly consistent in appearance - very loose, oily, black, organic, metallic (mainly iron oxide) waste mixed with sediment - but highly variable in moisture content (29 to 75%, weight of water to total weight), in-situ bulk density (1300 to 1650 kg/m³), and loss on ignition (7 to 31%). A simple laboratory procedure for preparing and monitoring stabilized sludge/sediment samples was developed that involved mixing with the selected quantities of stabilizing agents until consistent, sealed curing to maintain moisture conditions, and then monitoring compressive strength development with time at 20°C [9]. This approach is considered more representative of conditions in a large mass of solidifying material than open curing where significant strength development may be due to simple drying, rather than cementitious reactions.

Typical laboratory stabilization trials for a 46% moisture content sludge/sediment (combinations and proportions by weight, with 1, 7, 14 and 21 day penetrometer strengths in brackets) would include:

80% sludge/15% lime kiln dust (quick)/5% portland cement
(0.29, 0.43, >0.43, >0.43 MPa)

80% sludge/15% lime kiln dust (quick)/5% slag cement
(0.25, 0.31, 0.41, 0.43 MPa)

80% sludge/15% cement kiln dust (bypass)/5% portland cement
(0.04, 0.42, 0.43, >0.43 MPa)

80% sludge/15% lime kiln dust/5% portland cement
(0.12, 0.20, 0.22, 0.24 MPa)

80% sludge/15% fly ash (≈ 8% carbon)/5% lime kiln dust (quick)
(0.07, 0.12, 0.17, 0.18 MPa)

These results for stabilization trials meeting strength requirements for landfill and/or engineered fill indicated that the high organic content was not stopping pozzolanic and hydraulic reactions, but probably inhibiting them to some extent. Quick (i.e., unslaked) lime kiln dust is much more efficient than ordinary calcitic and dolomitic lime kiln dusts, or cement kiln dusts, and slag cements require alkaline activation. Major cementing compounds formed by the pozzolanic reactions are calcium silicate hydrates and low sulfate sulfoaluminate.

To check that miniaturization of the laboratory strength gain tests was valid, some large (90 kg) samples were prepared with various stabilizing agents. Both sealed curing and curing under a 0.8 m head of water were considered at a 7 to 13°C temperature range to simulate cooler field conditions. These tests, particularly submerged curing, supported the laboratory test methodology adopted.

Solubility Testing

The major environmental concern with any industrial sludge or contaminated sediment is the potential level of soluble toxic constituents, and their significance to fill design. However, there are a number of solubility testing procedures and acceptable toxic constituent levels to choose from [10-14]. The writer has adopted and modified an OECD [10] solubility test procedure as it gives the required solubility rate for each constituent of interest. Selection of the maximum allowable concentrations of toxic constituents is not easy as indicated by the range in Table 2 for various agencies.

The results for typical solubility tests on the raw and stabilized material are given in Table 3. Batch kinetics and desorption isotherms indicated a 1 g sludge/sediment to 0.05 ℓ distilled water ratio and 24 hour shaking to be appropriate. Unfortunately, the shaking at 3 Hz was rather aggresive, even on stabilized material, so there was continuous turbidty in the shaker flasks. After 24 hours, the shaker flask contents were allowed to settle, the supernatant drawn off and filtered, and the filtrate stored in a refrigerator until chemical anslysis. This was repeated four more times although only the first, third and fifth shaking results are given in Table 3.

The solubility data summarized in Table 3 indicate that the stabilization has reduced trace element constituent levels in all cases except copper and lead, but these are still well below the maximum allowable (EPA extract or Ontario industrial effluent in Table 2 for instance). While the alkalinity that results from the stabilization materials is important and very effective in limiting the solubility of many trace metals, this is probably not the case for copper and lead. Since the stabilized sludge/sediment was broken up before testing and then continually reduced during shaking (constant rates of solubility indicate this), the solubility test is far too severe to represent field conditions. A much gentler shaking action and column test are now used [11]. Cadmium is also considered in this solubility testing. Regardless, it is clear that the stabilized material is fully acceptable from an environmental viewpoint.

Field Trials

A rather efficient method was developed for large field trials that allowed a number of batches to be tested each day: a chute was constructed that allowed excavated material to be fed into a standard ready-mix truck; then the stabilizing agents were added using a small belt conveyor with the most reactive agent going in last to allow for visual control of initial stiffening; and after mixing, the batch was discharged at a location where strength monitoring could be completed on the stabilized material. Samples were also taken for laboratory testing. In several cases the stiffening was so rapid that water additions were necessary to get the stabilized material out of the ready-mix truck. After several days, it was possible to drive heavy vehicles onto the stabilized sludge/sediment. This ready-mix truck operation proved so efficient that it was adopted for full scale operations as an alternative to the large base stabilization plant that would have been required for the desired production rates.

Typical results for these field trials would include:

72.8% sludge/13.7% fly ash/8.1% lime kiln dust/5.4% portland cement
(0.41 MPa at 6 days)

83.6% sludge/12.9% lime kiln dust/3.5% portland cement
(0.28 MPa at 5 days)

75.7% sludge/11.5% fly ash/9.9% lime kiln dust/2.9% portland cement
(0.22 MPa at 5 days)

Full Scale Stabilization Process

Based on these types of field results, the final process (large ready-mix trucks with central additive storage silos) and stabilization agent selection (economics and availability, with waste quicklime kiln dust and slag cement favoured) were completed. A schematic of the process adopted is given in Figure 1. The optimum stabilization agents were determined to be 8 to 12% highly reactive quicklime kiln dust and 3 to 5% slag cement. This range of stabilization agents was necessary to handle variations in the sludge/sediment water content.

At peak operation, six 14 cubic yard ready-mix trucks were involved with about 1000 tonnes of material stabilized in an 8 hour shift. Following the successful stabilization of the sludge/sediment from the old harbour area, the process and plant were also used to stabilize a very soft sediment in another area of the plant. A similar fixed plant process is now being used to stabilize basic oxygen furnace clarifier sludge on a continuing basis. In each case, the stabilized product has been approved by the Ontario Ministry of the Environment for inert fill applications or landfilling, based on their unsaturated column leachate method. The physical properties of the stabilized products indicate they are suitable for earth borrow purposes. It is estimated that the stabilization cost was about $5.00 per tonne of stabilized material using byproduct binders.

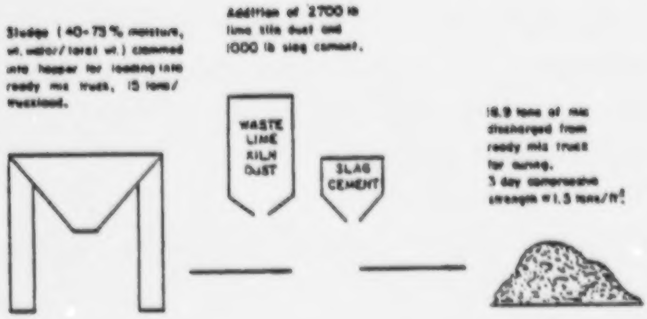
Sludge (40-75% moisture, wt. water/total wt.) clammed into hopper for loading into ready mix truck, 15 tons/truckload.
Addition of 2700 lb lime kiln dust and 1000 lb slag cement.
WASTE LIME KILN DUST
SLAG CEMENT
16.9 tons of mix discharged from ready mix truck for curing.
3 day compressive strength ≈1.5 tons/ft².

FIGURE 1 SCHEMATIC OF FULL SCALE STABILIZATION PROCESS

KILN DUST-FLY ASH STABILIZED BASE

The use of byproduct kiln dusts to replace hydrated lime as part of fly ash-kiln dust pozzolanic binder with aggregate in stabilized base for highway pavements offers materials and energy conservation benefits since conventional binders are replaced. There is considerable research in progress on kiln dust-fly ash stabilized base, with patent positions taken, and growing commercialization [1-3,15]. The writer's interest in such base stabilization initially involved three related problems: the influence of fly ash quality on the development of strength; the potential for using cement kiln dust and thermal plant sludges to replace hydrated lime; and the importance, if any, of aggregate type. Current work (Trow Ltd for Valley Forge Laboratories) involves the materials characterization aspects of a U.S. Federal Highway Administration study on the effectiveness of substituting a wide range of lime and cement kiln dusts for hydrated lime, with various fly ashes, in base stabilization.

Initial Studies

The writer's initial studies, in terms of materials used and strength development, are summarized in Table 4 [16]. Tests 1 to 3 show the influence of carbon content on strength development, with a dramatic decrease in strength at higher carbon contents. If a minimum compressive strength (without checking freeze-thaw resistance) of 6.9 MPa (1000 psi) is required, beneficiation to reduce the carbon content could be a critical factor in achieving this specified strength level. The lower strength for Test 3 shows the additional negative influence of an acidic fly ash. This is directly related to the need for an alkaline environment for pozzolanic reactions. Tests 1 and 4 to 6 indicate that blastfurnace slag is a somewhat better aggregate than limestone in the base stabilization process. This is undoubtedly related to the angular and closed vesicular nature of the slag, but there may also be a chemical factor related to the more alkaline environment with blastfurnace slag. Tests 7 to 9 involving byproduct limes were well below the minimum allowable strength generally adopted for base stabilization. However, this is to be expected since the quantity of free lime available was small compared with commerical hydrated lime. Increasing the amount of byproduct lime (ratio of byproduct lime to fly ash) would improve the strengths, and studies by others have provided the necessary technology [1-3].

Commercial Development

Following considerable research work, N-Viro Energy Systems of Toledo (Nicholson Concrete) have a patent position on cement kiln dust or lime kiln dust/fly ash/aggregate as a paving material and cement kiln dust/fly ash/water as a fill material [1-3,15]. A recent study to determine the usefulness, as stabilized base, of the cement kiln dust/fly ash/aggregate process has been reported to the Transportation Research Board [15]. Test sections of six different mixes containing cement kiln dust and fly ash as the cementitious ingredients,and crushed limestone as the aggregate,were constructed. Deflection measurements, monitoring of axle-load accumulations and compression tests of field samples were completed. After 25,820 equivalent 80 kN (18,000 lbf) single axle loads over 6 months, no cracking or surface damage was visible except in a localized area. The base was found to have the property of autogeneous healing. Anomalies in strength development were found with mixes containing portland cement addition and this may be related to the balance between hydraulic and pozzolanic reactions in terms of free lime availability. The overall study indicated that the cement kiln dust/fly ash/aggregate stabilized base is an important addition to highway construction technology and merits further development.

Federal Highway Administration Study

The current laboratory study is aimed at determining the effectiveness of substituting a wide range of kiln dusts for hydrated lime, for a number of fly ashes, in lime/fly ash/aggregate stabilized base. A total of 40 cement and lime kiln dusts from various plants, 16 representative fly ashes and 6 typical aggregates are involved. The kiln dusts and fly ashes are being characterized in terms of physical, chemical and mineralogical properties (chemical analyses by X-ray fluorence, mineralogical analyses by X-ray diffraction). Tests are also in progress to determine potential compressive strength development for various kiln dust-fly ash combinations (ASTM C593 - Fly Ash and Other Pozzolans for Use with Lime). Based on the results of the characterization program and proportioning studies, optimum kiln dust to fly ash ratios will be established for representative kiln dusts and fly ashes. Following this stage, optimum ratios will be determined for various kiln dust/fly ash/aggregate formulations. These mix combinations will be investigated to establish properties such as long-term strength, durability, volume stability, autogeneous healing and resilient modulus. It is anticipated that the study will result in recommended criteria for developing optimum kiln dust-fly ash ratios and designing acceptable mix compositions. Comments on, and input to, the study are welcomed.

CONCLUSION

There is a wide range of current and potential applications for cement kiln dusts and lime kiln dusts that provide significant materials and energy conservation benefits, and financial return, compared to the simple disposal option that is becoming more difficult with land and environmental constraints. While this review has focused on stabilization applications, it is anticipated that a fuller range of uses will develop as the necessary technical background is developed.

TABLE 1

TYPICAL RANGES OF CHEMISTRIES FOR KILN DUSTS, %

	Cement Kiln Dusts [1]			Lime Kiln Dusts [2]		
	Low	High	Average	Low	High	Average
SiO_2	6.0	28.5	16.5			
$A\ell_2O_3$	3.2	9.6	4.4	-	-	-
Fe_2O_3	0.8	5.9	2.7	-	-	-
CaO	16.0	65.0	47.6	35.6	43.4	38.6
MgO	0.8	4.8	2.3	25.4	32.2	28.6
SO_3	0.7	26.3	7.1	-	-	-
Na_2O	0.08	3.2	0.8	-	-	-
K_2O	1.08	26.2	5.5	-	-	-
LOI	2.50	32.0	16.0	22.9	36.4	29.1
S	-	-	-	0.2	1.0	0.7
CO_2	-	-	-	11.0	22.3	18.0
Available Lime	-	-	-	8.3	20.2	12.6

TABLE 2

TYPICAL MAXIMUM ALLOWABLE CONCENTRATIONS OF SUBSTANCES IN WATER

Maximum Level, mg/ℓ

Substance[a]	EPA Drinking Water Standards[b]	EPA Extract[c]	Ontario Drinking Water [MOE,13]	Ontario Industrial Effluent Discharges [MOE,12]
	Interim Primary			
Arsenic	0.05	5	0.05	
Barium	1.0	100	1.0	
Cadmium	0.01	1	0.01	0.001
Chromium (VI)	0.05	5	0.05	1.0
Fluoride	1.4-2.4		1.2-2.4	
Lead	0.05	5	0.05	1.0
Mercury	0.002	.2	0.002	0.001
			water quality	
Nitrate (as N)	10			
Selenium	0.01	1	0.01	
Silver	0.05	5	0.05	
	Secondary			
Chloride	250			
Copper	1			1.0
Iron	0.3			
Manganese	0.05			
Nickel				1.0
Sulphate	250			
Tin				1.0
Zinc	5			
pH	6.5-8.5			5.5-9.5

Notes:

a. Only ions and pH listed here. For pesticides, radioactivity, etc., see references cited.

b. EPA interim primary and proposed secondary drinking water standards. For full listing see EPA [14].

c. Extract based on EPA extraction procedure. Levels specified are 100 times the EPA national interim primary drinking water standards. For full details and listing see EPA [14].

TABLE 3

COMPARISON OF SOLUBILITY TEST DATA FOR RAW AND STABILIZED SLUDGE/SEDIMENT

Sample	Analysis of Filtrate, mg/ℓ											
	Ca	Cu	Fe	Hg	Mn	Mg	Ni	Pb	Zn	Cl	SO_4	pH
R-1	8.3	0.01	0.16	0.00032	0.08	2.5	0.02	<0.01	0.07	5.8	10.9	6.6
R-3	11.1	0.02	0.07	0.00011	0.57	1.5	0.03	<0.01	0.10	0.8	19.6	7.6
R-5	7.2	0.04	0.18	0.00012	0.71	2.2	<0.01	<0.01	0.37	1.3	24.7	7.4
S-1	160	0.04	0.06	0.00008	0.01	0.02	0.02	0.04	<0.01	9.0	2.9	11.9
S-3	81	0.02	0.06	0.00018	<0.01	0.06	<0.01	0.03	<0.01	7.0	1.4	11.5
S-5	111	0.04	0.06	0.00005	<0.01	0.03	<0.01	0.02	<0.01	9.1	3.4	11.7

Notes:

a. Using OECD [10] test procedure adopted. Solid (70 g) to distilled water (pH 6.4) ratio of 1 g to 0.05 ℓ. Cr <0.01 mg/ℓ in all cases.

b. Raw material R. R-1, R-3 and R-5 filtrates from first, third and fifth 24 hour shaking respectively.

c. Stabilized material S - 75% wet material/15% slag cement/10% lime kiln dust (quick), cured 77 days and crushed. S-1, S-3 and S-5 filtrates from first, third and fifth 24 hour shaking respectively.

TABLE 4

WASTE LIME-FLY ASH BASE STABILIZATION PROPORTIONS AND COMPRESSIVE STRENGTHS[a]

Test Number	Type of fly ash	% fly ash	% hydrated lime	% "waste" lime	% blastfurnace slag	% limestone aggregate	% water	Compressive Strength	
								MPa	(psi)
1	refined[b]	10	4	0	86	0	10	13.03	(1876)
2	normal[c]	10	4	0	86	0	10	7.68	(1105)
3	acid[d]	10	4	0	86	0	10	4.72	(680)
4	refined	10	4	0	70	16	10	11.58	(1666)
5	refined	10	4	0	60	26	10	10.76	(1548)
6	refined	10	4	0	0	86	8	8.63	(1242)
7	normal	10	0	4[e]	86	0	10	1.47	(212)
8	normal	10	0	4[f]	86	0	10	1.17	(168)
9	normal	10	0	4[g]	86	0	10	1.10	(159)

NOTES:

a. Three 102 mm diameter (4") specimens prepared by modified Proctor procedure, cured in double plastic bags at 38±2°C for 7 days (procedure closely parallels ASTM C593 except for higher compactive effort).

b. Beneficiated fly ash, carbon content ≈6-7%.

c. Unbeneficiated fly ash, carbon content ≈11-13%.

d. Acidic unbeneficiated fly ash, carbon content ≈12%.

e. Cement kiln dust.

f. Scrubber sludge in slurry form (% weight based on solids), thermal electric plant.

g. Scrubber sludge in dry form, thermal electric plant.

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SYMPOSIUM

FLY ASH IN 2ND GENERATION CONCRETE

G.E. BROWN

DUFFERIN CONCRETE PRODUCTS
ISLINGTON, ONTARIO

MINERAL FILLERS

Joint ORF/Canmet Symposium, Toronto, October 20 & 21, 1981

FLY ASH IN 2nd GENERATION CONCRETE

by G. E. Brown

FLY ASH IN 2nd GENERATION CONCRETE

Introduction

Fly ash has been used in concrete throughout the world for some 30 to 40 years, although it wasn't introduced here in Ontario until about 1970. Prior to this time, the use of fly ash in concrete lay dormant for some 1900 years, since the time of the Romans. Many structures constructed by the Romans are still standing today attesting to the durability and permanence of fly ash concrete. Apart from the fact that some Roman construction has withstood the erosion from the sea and rivers for some 2000 years, the more recent research conducted on fly ash concrete well documents the fact that fly ash does, in fact, possess many advantageous features.

Although the theme of this symposium is "mineral fillers", we cannot accept the word "filler" when associated with fly ash in concrete as fly ash is very active both chemically and physically. As will be reviewed later, many of the advantageous characteristics of concrete are greatly improved when fly ash is used.

We, in Dufferin Concrete Products, have capitalized on these features and market our fly ash concrete as one containing not a filler, but a high quality, CSA approved material possessing tremendous engineering qualities which extend to us marketing capabilities not previously available. An added bonus is the fact that the fly ash, a low cost by-product, is replacing a very high energy intensive material, cement: and as each year passes with its higher oil prices, the economic advantage becomes more prominent.

Physical and Chemical Properties

Slide No. 1 represents a 4000 x magnification photograph of a particle of cement and a particle of fly ash. First of all, you will note that the cement, being a product of a grinding process, is very angular as opposed to the spherical shape of the fly ash. Although the fineness of cement and fly ash is similar, the shape of the particles plays an important role in concrete. When millions of these spherical shaped pieces of silica/alumina are added to concrete they act as ball bearings and reduce internal friction and thus increase the flowability and placeability of concrete. A secondary mechanism to consider is the fact that the cement particles react immediately when wetted with water and the already rough surface of each particle increases internal friction as this surface starts to turn to gel during the hydration process. Conversely, the spherical pieces of fly ash are inert at this stage during the placement of the concrete and continue to act as a lubricant by the ball bearing effect of their shape. We will discuss more of the advantages produced by the physical properties of fly ash later and would like to explain chemically how fly ash works in concrete.

Figure No. 1 shows a comparison of a typical oxide analysis on normal portland cement and fly ash. When cement hydrates, an abundance of calcium hydroxide or free lime is liberated through the hydration of the tricalcium silicate. It can be seen from the chemical analysis that the fly ash is predominantly silicious in nature and, therefore, reacts with the calcium hydroxide to form stable cementitious compounds. This lime pozzolan reaction produces a calcium silicate hydrate very similar to the C_2S hydrate, with less coarse pores and lower permeability. This is a major contributing factor for increased density and reduced permeability; two extremely important criterion for durability.

Fly Ash, The Ingredient

Fly ash is a by-product of coal burning steam generating plants. Most of the fly ash utilized here in Ontario is a product from the Hydro Lakeview Generating Station located near the south end of Highway 427 in the west part of Toronto. The fly ash is composed of spheres of silica and alumina and is actually the non-combustible impurities found in coal. These impurities are carried from the combustion chamber in liquid form and upon cooling in air, form spherical particles that are in turn collected in electrostatic precipitators. Due to more rigid air pollution control standards levied in the last 20 years, electrostatic precipitators were installed at each of the eight units at Lakeview. These electrostatic precipitators consist of hundreds of electrically charged fine wires that are installed in the stream of combustion materials leaving the boilers. An automatic system momentarily cuts the power on some of the wires, leaving most of the wires electrically charged. When the power is cut, the particles of fly ash that were adhering to them drop down into a bin that collects the fly ash. The system works continuously with different banks of wires having the electricity momentarily stopped and in this way the collection is continuous.

All fly ash collected at this station is collected utilizing a selective withdrawal system which depends on the load and effeciency of each steam generator. In this way, carbon content of the fly ash can be reasonably well controlled. When each truck load of fly ash is loaded and sent over the scales a sample is taken immediately and analysed for carbon content and fineness utilizing some unique and advanced laboratory equipment and techniques. The results of each of these two tests are marked on the delivery bill so that each ready mix concrete company will have actual test results of the material before it is pumped into their silos. No other component used in concrete is tested to this extent. In addition to these tests, the chemical and physical properties of the fly ash are being tested continuously by Ontario Hydro to ensure its conformity with CSA CAN3-A266.3-M78 specifications.

Marketing

After gaining a thorough understanding of the chemical and physical properties of fly ash concrete, there emerges an embryo for a research and marketing concept never before exploited. A tabulation of some of the more interesting characteristics of fly ash concrete reveals the following:

(a) long term strength gain between 28 and 90 days
(b) increased density
(c) increased workability
(d) improved finishability
(e) improved pumpability
(f) reduced thermal volume change
(g) reduced permeability
(h) increased sulphate resistance

A great deal of information can be obtained from the many publications available on fly ash concrete. A quick, concise source is CSA Special Publication CAN3-A266.4-M78.

Following several years of study and research, Dufferin Concrete Products developed a marketing strategy utilizing all the documented improved characteristics of fly ash concrete. We market these products under our Advanced Concrete Technology Systems, "ACTS". We offer eight different concrete products, most of which utilize fly ash in their production. To illustrate the effective utilization of these unique engineering characteristics in our marketing strategy, we present the following examples.

The Products

Figure No. 2 represents a comparison between typical strength gain curves of normal portland cement concrete and fly ash concrete. Due to the continuing pozzolanic reaction, the fly ash concrete continues to gain appreciable strength up to and beyond 90 days.

90 Day Concrete

Our company is now marketing special mixes that are formulated to reach the designed strength in 90 days. For example, on many high rise projects, the columns need not reach the design strength in 28 days due to the construction progress. On many, the full loading will not take place for many months, when the entire building frame is completed. On a large cross sectional column of high strength concrete, why specify 28 day strengths when 90 day concrete will suffice? Two advantages become apparent in favour of 90 day concrete. Firstly, the heat of hydration will be lower with 90 day fly ash concrete, thus reducing thermal stress and possible thermal shock during winter construction and, secondly, a lower cost concrete can be used.

The same principal is applied where large raft foundations are being constructed. Here is a prime example of where heat of hydration and thermal stress are of major concern to the design engineers. Since the foundations won't receive their full load for many months, a 90 day fly ash concrete is utilized saving the owner money and helping to solve the thermal stress problem at the same time.

We cannot take credit for this technology. In Chicago, for instance, 90 day concrete has been used for some time now. However, Canada was one of the last countries in the world to utilize fly ash in the Commercial Ready Mix Industry, and some of this technology is just starting to be utilized effectively by Ready Mix suppliers.

Sulfo-Krete

Throughout the Niagara Peninsula and Hamilton, with isolated instances in various other parts of the province, sulfates in groundwater will react with normal portland cement concrete. These sulfates are either natural, or artificial through chemical waste disposal. When a normal concrete not designed for sulfate resistance is placed in these environments, a disintergration of the concrete occurs. It may be caused by either of two reactions. One is the reaction between the sulfate in the groundwater and calcium hydroxide to form calcium sulfate, or gypsum, and the other is a reaction between the sulfate and the reactive alumina-bearing phases in hardened cement to produce calcium sulfoaluminate, or deleterious ettringite. The products of both reaction occupy a greater volume and disintergration occurs.

For this reason, special cements are produced primarily meeting maximum values for tricalcium aluminate. In North America two types are available at relatively high cost to normal portland. Availability of proper raw materials for this cement production is sometimes difficult and the demand for the cement is sporadic and low as compared to predictable sales for normal portland.

It has been known for many years that fly ash increases sulfate resistance. Utilizing all available research on this subject, we formulated and proof tested special sulfate resistant concretes containing fly ash and lower cost cements than would be otherwise specified. These blends are marketed under the name Sulfo-Krete.

Floor Krete

When fly ash is used in concrete it adds tremendous flowability and finishability and properly designed floor mixes will exhibit much better finishing characteristics than concrete not containing a fly ash. During winter construction, for example, where setting times are likely to be affected by cool temperatures, the fly ash can be used as an additive to give the properties noted above. Or, utilizing accelerators, some cement replacement can be achieved without altering setting and giving superior finishability. In additon, due to the long strength gain characteristics, a stronger, denser, more serviceable floor is produced. We market this concrete as Floor Krete.

Pumping

Fly ash can be used as a pumping aid on relatively lean mixes. Until the advent of fly ash, normal practice dictated the addition of extra cement to a mix to make it pump. For instance, a 20 MPa mix would actually satisfy a 25 or 30 MPa specification, the extra cement merely being utilized as a pumping aid. Good fly ash pump mix designs now utilize the fly ash as a pumping aid leaving the required cement in the mix to achieve the design strength.

K-Krete

K-Krete is not a concrete, but a controlled density fill composed of cement, fly ash, a filler material such as concrete sand, and water. K-Krete is used where conventional back-fill materials pose problems; for instance, for quick placement of fill under access routes where normal compaction time would not be fast enough to meet critical schedules. Back-fill under large pipes with K-Krete guarantees 95% Standard Proctor compaction, where, with conventional back-fill, obtaining the required compaction in these tight quarters would be virtually impossible.

Summary

Fly ash, where properly use, represents, without a doubt, an economic ingredient to concrete that improves virtually every characteristic of commercial concrete.

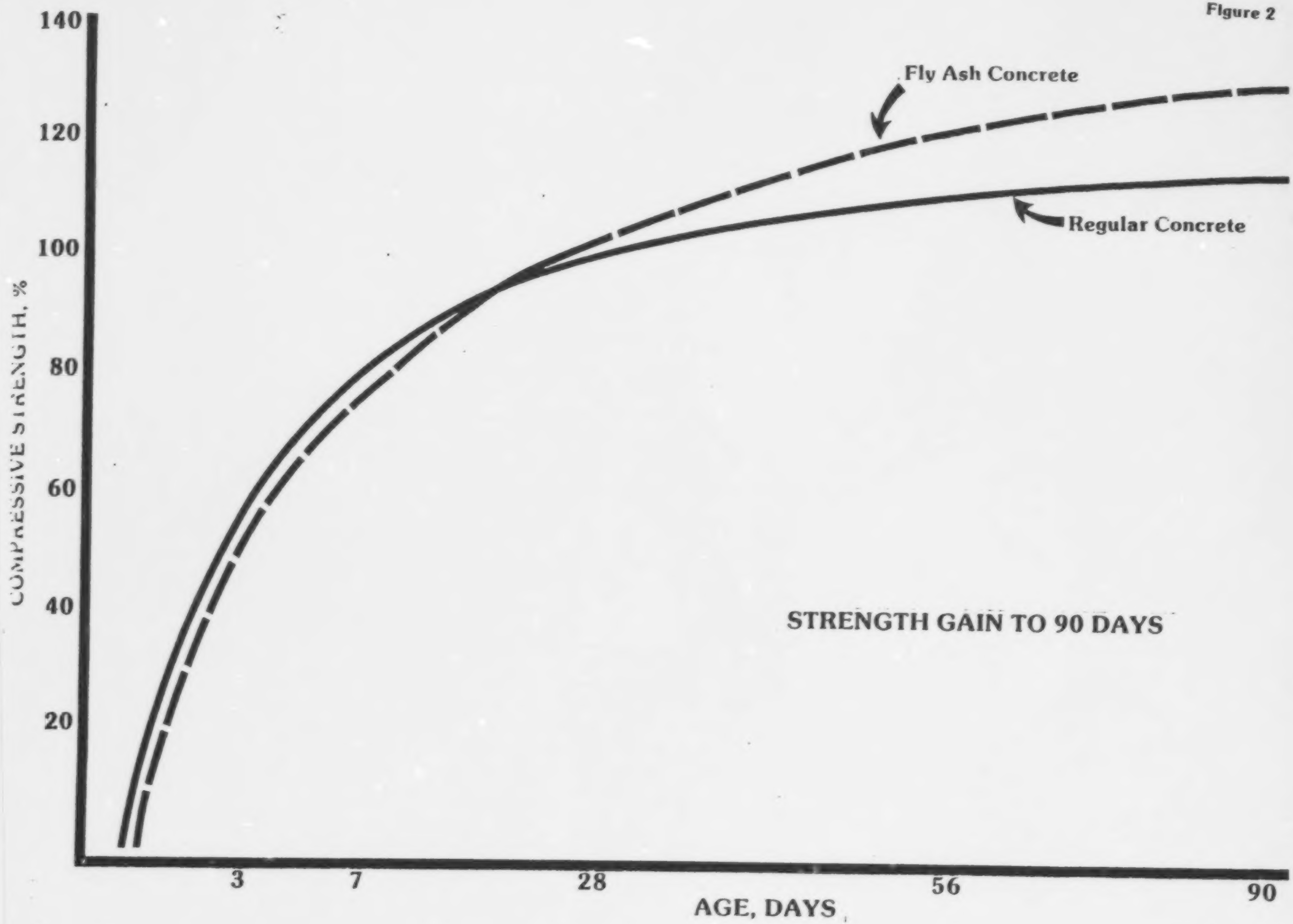
Upon examination of these individual improved characteristics, there evolves sound criteria for an unique marketing strategy, of which we have taken advantage.

FIGURE 1

CHEMICAL COMPARISON

	NORMAL PORTLAND CEMENT	FLY ASH
CaO	63	4
SiO_2	21	44
Al_2O_3	6	26
Fe_2O_3	2	9
MgO	3	1
SO_3	3	1

Figure 2



STRENGTH GAIN TO 90 DAYS

File 135
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USE OF FLY ASH IN CLAY BRICK MANUFACTURING

H. PENN

BRAMPTON BRICK LIMITED
BRAMPTON, ONTARIO

USE OF FLY ASH IN CLAY BRICK MANUFACTURING

BY HOWARD PENN

ORF/CANMET SYMPOSIUM, TORONTO

21ST OCTOBER 1981

THE ESCALATING INCREASE IN ENERGY COSTS, PARTICULARLY NATURAL GAS, HAS FORCED US AT BRAMPTON BRICK LIMITED TO SEEK WAYS TO EFFICIENTLY UTILIZE OUR ENERGY CONSUMPTION AND RESEARCH ENERGY CONSERVATION PROGRAMS. THIS PARTICULAR PROGRAM INVOLVES THE UTILIZATION OF FLY ASH AS A BODY ADDITIVE, IN THE MANUFACTURE OF A STRUCTURAL CLAY BRICK. THERE IS NOTHING NEW ABOUT MIXING ASHES RESULTING FROM THE BURNING OF COAL WITH CLAYS FOR BRICKMAKING. THIS HAS BEEN DONE SINCE THE 17TH CENTURY FOR THE MANUFACTURE OF STOCK BRICKS, THE MOTIVES FOR DOING SO BEING TO REDUCE THE SHRINKAGE OF THE CLAY AND TO MAKE USE OF THE HEATING VALUE OF THE UNBURNT CARBON IN THE ASHES.

FLY ASH IS ONE OF THE TWO TYPE OF ASH (THE OTHER BEING BOTTOM ASH) PRODUCED DURING THE GENERATION OF ELECTRICITY IN COAL FIRED GENERATING STATIONS. IT IS A LIGHT AIRBORNE PARTICULATE WHICH IS CARRIED OUT OF THE BOILER IN THE FLUE GASES AND IS REMOVED BY HIGHLY EFFICIENT ELECTROSTATIC PRECIPITATORS AND COLLECTED IN DRY STORAGE SILOS OR SLUICED TO LAGOONS. BOTTOM ASH, ON THE OTHER HAND, IS A COMBINATION OF HEAVIER ASH PARTICULATE AND MOLTEN SLAG WHICH FORMS ON THE INTERNAL SURFACES OF THE BOILER AND COLLECTS IN THE BOTTOM WHERE IT IS ROUGH GROUND TO AID IN ITS REMOVAL AND SLUICED BY HIGH PRESSURE WATER JETS TO EITHER HOLDING BINS OR LAGOONS.

FLY ASH IS COMPOSED LARGELY OF COMPOUNDS OF SILICA, ALUMINA, IRON, LIME AND CARBON TOGETHER WITH SAMLLER QUANTITIES OF MAGNESIA, TITANIUM, POTASSIUM, SULPHUR AND ALKALI COMPOUNDS.

FROM A PHYSICAL STANDPOINT, FLY ASH IS GLASSY RATHER THAN CRYSTALLINE DUE TO ITS THERMAL HISTORY.

FLY ASH PARTICLES ARE TYPICALLY SPHERICAL AND RANGE IN SIZE FROM ONE TO 150 MICRONS WITH A MEAN DIAMETER OF 6 TO 9 MICRONS. IRON IS PRESENT BOTH AS MAGNETIC AND NON-MAGNETIC OXIDES. CARBON PARTICLES IN THE FLY ASH TEND TO BE SOMEWHAT COARSER AND MORE ANGULAR THAN THE AVERAGE PARTICLE SIZE. IN CONTRAST TO FLY ASH, BOTTOM ASH IS TYPICALLY GREYISH BLACK IN COLOUR, QUITE ANGULAR AND IRREGULARLY SHAPED.

THE BOTTOM ASH PARTICLES ARE SOMEWHAT POROUS AND RANGE FROM THREE-QUARTERS GRAVEL TO A PARTICLE SIZE PASSING 200 MESH, PRESENTING A COMPOSITE MATERIAL SIMILAR TO THAT OF A CLASS B AGGREGATE. IT CAN ALSO BE SEEN IN THIS SLIDE THAT FLY ASH IS IN THE SAME GRAIN SIZE DISTRIBUTION AS CLAY AND SILT.

THE FIRST TASK AT BRAMPTON BRICK LIMITED WAS TO CONDUCT A THOROUGH LITERATURE SEARCH. THE RESULTS OF THIS SEARCH PROVIDED A LIST OF INDIVIDUALS WHO ARE PRESENTLY USING FLY ASH IN CLAY BRICK ON A PRODUCTION BASIS OR HAVE HAD EXPERIENCE IN THE PAST. SUCCESSFUL LINES OF CONTACT WERE ESTABLISHED AND SUBSEQUENT ONSITE TECHNOLOGICAL EXAMINATION FOLLOWED.

AT PRESENT FLY ASH IS USED IN ENGLAND, CZECHOSLOVAKIA, POLAND AND RUSSIA AS AN ADDITIVE AS WELL AS A BASIC COMPONENT OF THE PRODUCTION CLAY. BENEFITS ACHIEVED FROM THIS ADDITION ARE HIGH STRENGTH, LOWER BULK DENSITY, IMPROVED DRYING BEHAVIOUR AND REDUCTION OF THE SPECIFIC HEAT CONSUMPTION ON FIRING.

THE FIRST STOPOVER ON OUR ITINERARY WAS ENGLAND, THE BUILDING RESEARCH STATION IN WATFORD. A MAJOR RESEARCH PROGRAM WAS CONDUCTED REGARDING THE USE OF FLY ASH IN CLAY BRICK PRODUCTION IN THE 1960'S. THIS INCLUDED LABORATORY TRIALS, EXPERIMENTAL FIRING IN INDUSTRIAL KILNS AND EXPOSURE TEST DATA OVER A TEN YEAR PERIOD. THE CONCLUSIONS OF THESE TESTS INDICATED THE FLY ASH MAY BE ADDED TO MANY CLAYS TO PRODUCE BRICKS OF GOOD DURABILITY FOR NORM , BUILDING PURPOSES.

THE FOLLOWING SLIDES SHOW A SERIES OF FLY ASH CLAY TEST PIERS WHICH HAVE BEEN IN PLACE FOR OVER SIXTEEN YEARS. VARIOUS PERCENTAGES OF FLY ASH HAVE BEEN ADDED TO A WIDE VARIETY OF CLAYS FROM ENGLAND.

ANOTHER STOPOVER IN ENGLAND INCLUDED A BRICKWORKS WHICH IS PRESENTLY CONSUMING 30,000 METRIC TONS OF FLY ASH ANNUALLY TO PRODUCE 35 MILLION BRICKS. THE BENEFITS REALIZED BY THIS COMPANY ARE TWO FOLD------FIRSTLY, SAVINGS IN THE KILN ENERGY CONSUMPTION AND SECONDLY AS A GROGGING AGENT IN REPLACEMENT OF PURCHASED SAND.

THE NEXT STOPOVER ON OUR ITINERARY WAS CZECHOSLOVAKIA. MEETINGS WERE HELD WITH REPRESENTATIVES FROM THE RESEARCH INSTITUTE OF BUILDING MATERIALS IN PRAGUE. HIGHLIGHTS OF THE MEETING WERE:

1. IN CZECHOSLOVAKIA APPROXIMATELY FIFTEEN MILLION TONS OF FLY ASH IS AVAILABLE EACH YEAR. AS A RESULT UTILIZATION OF THIS WASTE PRODUCT HAS BECOME ESSENTIAL. ALTHOUGH THE USE OF FLY ASH IN BRICK PRODUCTION WILL NOT COMPLETELY ELIMINATE THIS PROBLEM, THE BRICK INDUSTRY CAN EFFECTIVELY CONTRIBUTE AND AT THE SAME TIME IMPROVE SOME ASPECTS OF TECHNOLOGY FOR THE MANUFACTURE OF BRICK.

2. THE MAJOR BENEFITS REALIZED FROM THE USE OF FLY ASH ARE A DECREASE IN UNIT WEIGHT, A DECREASE IN DRYING TIME, A DECREASE IN SHRINKAGE AND A DIRECT ENERGY SAVINGS IN THE FIRING PROCESS.

A TRIP TO A BRICK MANUFACTURING PLANT IN NORTHERN BOHEMIA, DEMONSTRATED A PLANT CONSUMING 40,000 METRIC TONS OF FLY ASH ANNUALLY TO PRODUCE 45 MILLION BRICK UNITS. THE DIRECT MEASUREABLE BENEFITS REALIZED AT THIS PLANT WERE A REDUCTION IN SHRINKAGE, IMPROVED FINISHED QUALITY AND REDUCED FUEL CONSUMPTION.

THE LAST LEG OF OUR JOURNEY TOOK US TO POLAND. OUR STOPOVERS THERE INCLUDED THE CERAMIC RESEARCH BUREAU IN WARSAW AND THE ACADEMY OF CERAMIC ENGINEERING AT THE UNIVERSITY OF CRAKOW.

IN POLAND 25 PERCENT OF THE BRICK PLANTS ARE USING GLY ASH AS A COMPONENT OF THE CLAY MIXTURE IN VARYING AMOUNTS. LAST YEAR 400,000 TONS OF FLY ASH WERE CONSUMED BY THE BRICK INDUSTRY.

PRESENTLY, FLY ASH IN POLAND IS USED AT TWO ADDITION RATES. THIRTY PERCENT BY VOLUME AS A BODY ADDITIVE AND FIFTY PERCENT BY VOLUME AS A BASIC COMPONENT.

CURRENT DESIGNS ARE ON STREAM FOR THE CONSTRUCTION OF A BRICK PLANT UTILIZING FLY ASH AT A 70 PERCENT BY VOLUME ADDITION RATE. THIS PLANT WILL BE LOCATED ADJACENT TO A POWER GENERATING STATION SO THAT THE FLY ASH CAN BE DIRECTLY CONVEYED TO THE PLANT.

FLY ASH IS ALSO BEING USED IN MANY OTHER BUILDING PRODUCTS IN POLAND, SUCH AS CONCRETE BLOCKS, DRAIN TILE, AND LIGHTWEIGHT AGGREGATE.

THE CONCLUSIONS DRAWN FROM THIS SEARCH ARE THAT THE TECHNOLOGY DOES EXIST, IT HAS BEEN PROVEN AND THE BENEFITS OF AN ECONOMICAL NATURE ARE REALISTIC TO THE USER IN COMPARISON TO ALTERNATE MATERIALS.

RESEARCH WAS INITIATED AT BRAMPTON BRICK LIMITED TO DETERMINE THE COMPATIBILITY OF THE FLY ASH SHALE MIXTURES. THIS PROGRAM INVOLVED TESTING VARIOUS VOLUME ADDITION RATES AND CARBON RANGES. THE TESTING PROGRAM COMPRISED OF RAW MATERIAL CHARACTERIZATION, A VARIETY OF THERMAL ANALYSES FOLLOWED BY A COMPLETE SERIES OF QUALITY ASSURANCE TESTS. RESULTS OF THE TESTS MENTIONED ABOVE WERE A REDUCTION IN TOTAL SHRINKAGE, INCREASED ABSORPTIONS, AND A DECREASE IN BULK DENSITY.

THUS, THE INITIAL RESEARCH SHOWED FAVOURABLE POTENTIAL RESULTS AND A GREEN LIGHT WAS GIVEN FOR A MINI PRODUCTION TRIAL.

TRUCKLOADS OF FLY ASH WERE DELIVERED BY DUMP TRUCKS AND STOCKPILED AT THE SITE. A SMALL BUCKET LOADER WOULD FEED THE FLY ASH TO A SCREW CONVEYOR HOPPER. THE SCREW CONVEYOR WOULD SUPPLY THE FLY ASH ONTO THE BELT FEEDING THE PUGMILL PRIOR TO THE EXTRUDING MACHINE.

TO EVALUATE THE EFFECT OF THE FLY ASH SHALE MIXTURE DURING THE PRODUCTION TRIAL, THE EXTRUSION RATE AND LOAD ON THE EXTRUDER MOTOR WERE RECORDED WHILE SAMPLES WERE TAKEN BEFORE AND DURING THE ADDITION OF FLY ASH.

SAMPLES WERE TAKEN ON A REGULAR BASIS, THEN WEIGHED AND TESTED FOR GREEN STRENGTH, DRY STRENGTH AND SHRINKAGE.

THE NEXT STEP WAS TO FOLLOW THE PRODUCTION STEPS AND MONITOR THE DRYING AND FIRING CONDITIONS.

IN ORDER TO EVALUATE THE EFFECT OF FLY ASH SHALE BRICK IN THE FIRING PROCESS A TRAVELLING THERMOCOUPLE WAS CONNECTED TO ONE OF THE KILN CARS WITH FLY ASH SHALE BRICK.

AFTER HAVING EXITED THE KILN THE BRICK WERE SAMPLED FROM VARIOUS POSITIONS ON THE CAR. THE SAMPLES WERE THEN CUT IN HALF AND PREPARED FOR A SERIES OF QUALITY ASSESSMENT TESTS TO EVALUATE THE DURABILITY OF THE UNITS. THESE TESTS INCLUDED VARIOUS ABSORPTION TEST, COMPRESSION TESTS, A TEST FOR EFFLORESCENCE AND FREEZE THAW TESTING.

THE RESULTS WERE THEN TABULATED AND THE FOLLOWING CONCLUSIONS DRAWN FROM THIS PRODUCTION TRIAL.

THERE ARE SIX POTENTIAL BENEFITS FROM A FLY ASH SHALE BRICK.

THE MAJOR FORECAST BENEFIT IS DIRECTLY RELATED TO ENERGY CONSERVATION - FUEL SAVINGS IN THE FIRING PROCESS. THE ACTUAL HEAT REALIZED IN MANUFACTURE MAY BE CONSIDERABLY LESS THAN THE THEORTICAL HEAT OF THE CARBON BURNOUT. THE DIFFERENCE IN YIELD DEPENDS ON SUCH FACTORS AS THE PERMABILITY OF THE BRICK, THE OXYGEN CONTENT OF TH KILN ATMOSPHERE, THE VELOCITY OF THE KILN GASES, PARTICLE SIZE OF THE FUEL, THE SCHEDULE OF FIRING AND THE EASE OF COMBUSTION.

THE ADDITION OF THE FLY ASH TO THE RAW MATERIAL ALLOWS FOR A REDUCTION IN MINING AND PROCESSING OF NATURAL RESOURCES. THIS MAJOR ECOLOGICAL BENEFIT IS IN KEEPING WITH THE CLIMATE OF PUBLIC OPINION IN TODA'S ENVIRONMENT BY RECYCLING INDUSTRIAL WASTE MATERIAL.

THE BURN OUT OF THE CARBON IN THE FLY ASH RESULTS IN A REDUCTION IN UNIT WEIGHT. THIS IN TURN HAS MANY SPIN OFFS, WHICH INCLUDE TRUCKS HAULING LESS WEIGHT, AND AS A RESULT REDUCED GASOLINE CONSUMPTION AS WELL AS LESS OVER THE HIGHWAY LOADS WITH POSSIBLE LESS ROAD WEAR AND TEAR.

THE DURABILITY TESTS CONDUCTED ON THE FIRED BRICK INDICATED LOWER SATURATION COEFFICIENTS AND HIGHER STRENGTHS AS WELL AS WITHSTANDING ACCELERATED TEST METHODS FOR FREEZE THAW TESTING.

THE SPHERICAL SHAPE OF THE FLY ASH PARTICLES ACTS AS A LUBRICATING AGENT IN THE FLY ASH SHALE MIX DURING THE EXTRUSION PROCESS. THIS RESULTS IN A DECREASE IN POWER CONSUMPTION DURING THIS STAGE OF PROCESSING.

THE SIXTH BENEFIT IS THE DEVELOPMENT OF NEW LINES OF BRICK, FOR EXAMPLE FLY ASH BRICK.

IN THE FUTURE, WE AT BRAMPTON BRICK HOPE TO PROGRESS TO OBTAIN THE MAXIMUM EFFICIENCY OF THE FLY ASH THROUGH MASS UTILIZATION.

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VALORIZATION OF CONDENSED SILICA FUME FROM SILICON AND FERROSILICON PLANTS

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VALORIZATION OF CONDENSED SILICA FUME FROM
SILICON AND FERROSILICON PLANTS

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presented at the
Seminar of Mineral Fillers
Toronto

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1. INTRODUCTION

With recent environmental regulations, industries are obliged to collect and to dispose of all by-products in a safe way. This apply especially to the large quantities of fine powders that are now collected by electrostatic precipitators, in bag-houses, or in any other sophisticated and costly de-dusting installations.

On the other hand, a lot of finely ground powders are presently used by various industries. However, due to recent increases in the price of energy, the large scale grinding of industrial minerals is becoming increasingly expensive, thus it is of interest to try to use various very fine by-products that are already in powder form.

Sometimes, fortunately, some by-products easily fulfill the specifications of other industries without any further processing or benefication; the use of fly ash in the concrete industry is a good example of such an ideal situation.

However, quite often it does not work so well because available by-products do not meet very specific user requirements. Very often de-dusting operations have been designed to provide for the low cost removal and disposal of fine material without any consideration of potential markets. At such installations, any transformation of the de-dusting operation is costly and the by-product producer is not interested in investing large sums of money to adapt his by-product to the needs of potential customers because the pay back is generally very low and there is no match between the amount of product available and customer needs. Also, powders that could be of interest to some industries may be too fine to be handled economically or may create severe dust problems for both the producer and the customer. In such cases the customer is not interested in investing in costly bag-house collecting system to solve this problem. It often is more economical to continue to buy ground raw material for his special needs from established sources. Thus, it is not always easy to match the needs of an industry that is presently using a powder with a more or less similar waste by-product powder generated by another industry.

The valorization of condensed silica fume, a by-product of the fabrication of silicon or ferrosilicon alloys will be discussed in this presentation.

2. GENERATION AND CHARACTERISTICS OF CONDENSED SILICA FUME

Few industrial process generate particles as fine as the condensed silica fume from silicon and ferrosilicon open electric arc furnaces. This powder is so fine and so difficult to handle than the producers have always been discouraged in their efforts to find potential market even they were aware that this material had good potential for many applications. The problem was so crucial that in 1975 an award of 10 000 Swiss Francs (6 000 $) was offered by the I.P.F.E.O. (Institut des Producteurs de Ferro-alliages d'Europe Occidentale), to anyone that could find a solution to this problem (1).

2.1 Formation and capture

Condensed silica fume is produced during the reduction of quartz by coal. The reduction of the quartz to silicon is not direct and an intermediate gaseous suboxide of silicon, SiO, is produced in a certain zone of the furnace as shown in Figure 1. Some of this SiO gas is entrained with the other combustion gas in the stack. The SiO is oxidized and condensated in air and forms very tiny microspheres of vitreous silica.

Most of the condensed silica fume particles have a diameter smaller than 1,0 μm. The average diameter is about 0,1 μm which is 100 times finer than an average cement or fly ash particle. When observed at high magnification they are seen in the form of perfect spheres, Figure 2. At higher magnification they appear to have a rather raspberry type surface, Figure 3.

The current practice is to collect condensed silica fume in bag-houses and to dispose of them by wetting in dumps.

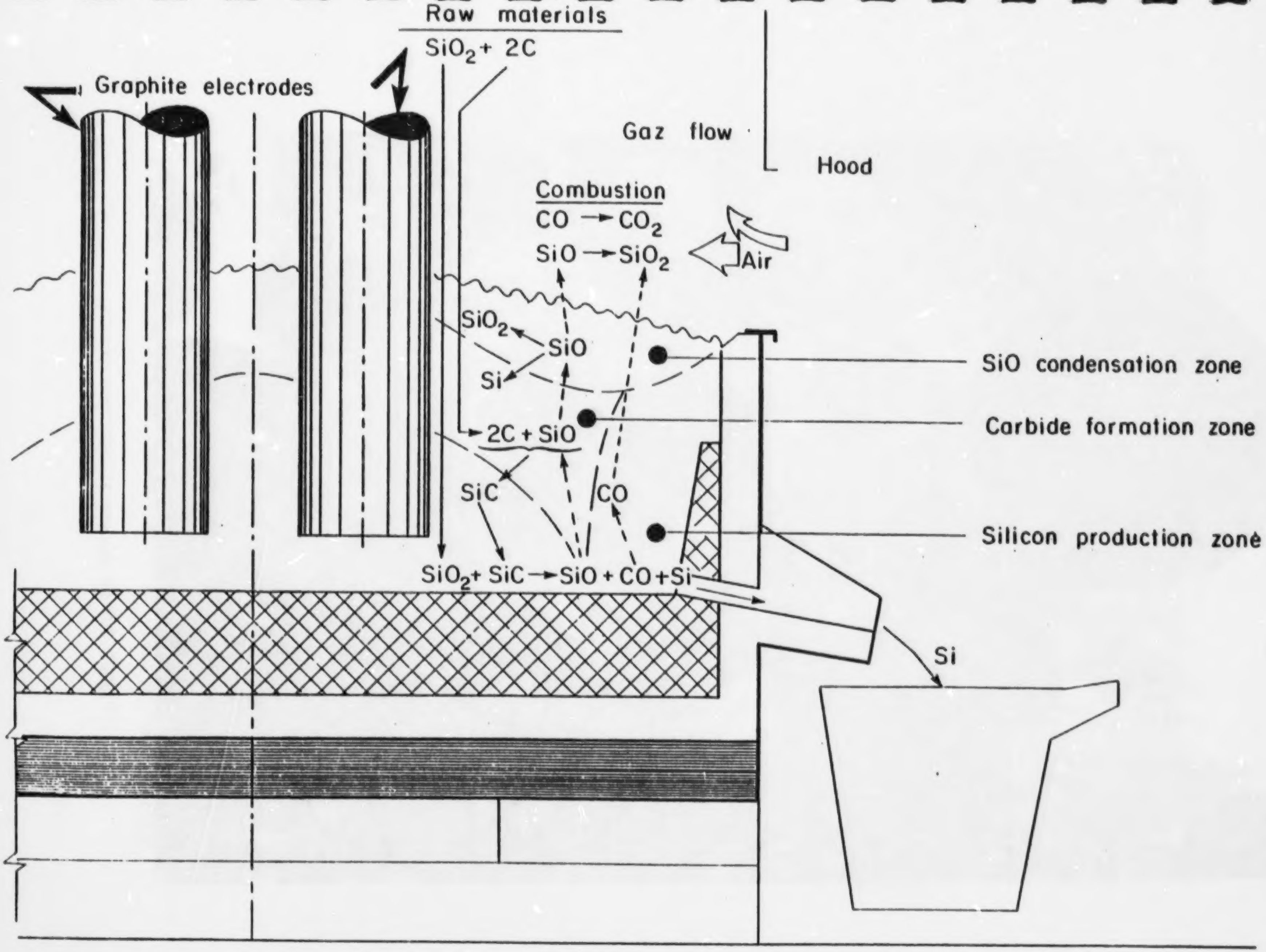
Raw materials
$SiO_2 + 2C$
Graphite electrodes
Gaz flow
Hood
Combustion
$CO \rightarrow CO_2$
$SiO \rightarrow SiO_2$
Air
SiO_2
SiO
Si
$2C + SiO$
SiC
CO
$SiO_2 + SiC \rightarrow SiO + CO + Si$
SiO condensation zone
Carbide formation zone
Silicon production zone
Si

FIGURE I_ GENERATION OF CONDENSED SILICA FUME (S.K.W. documentation)

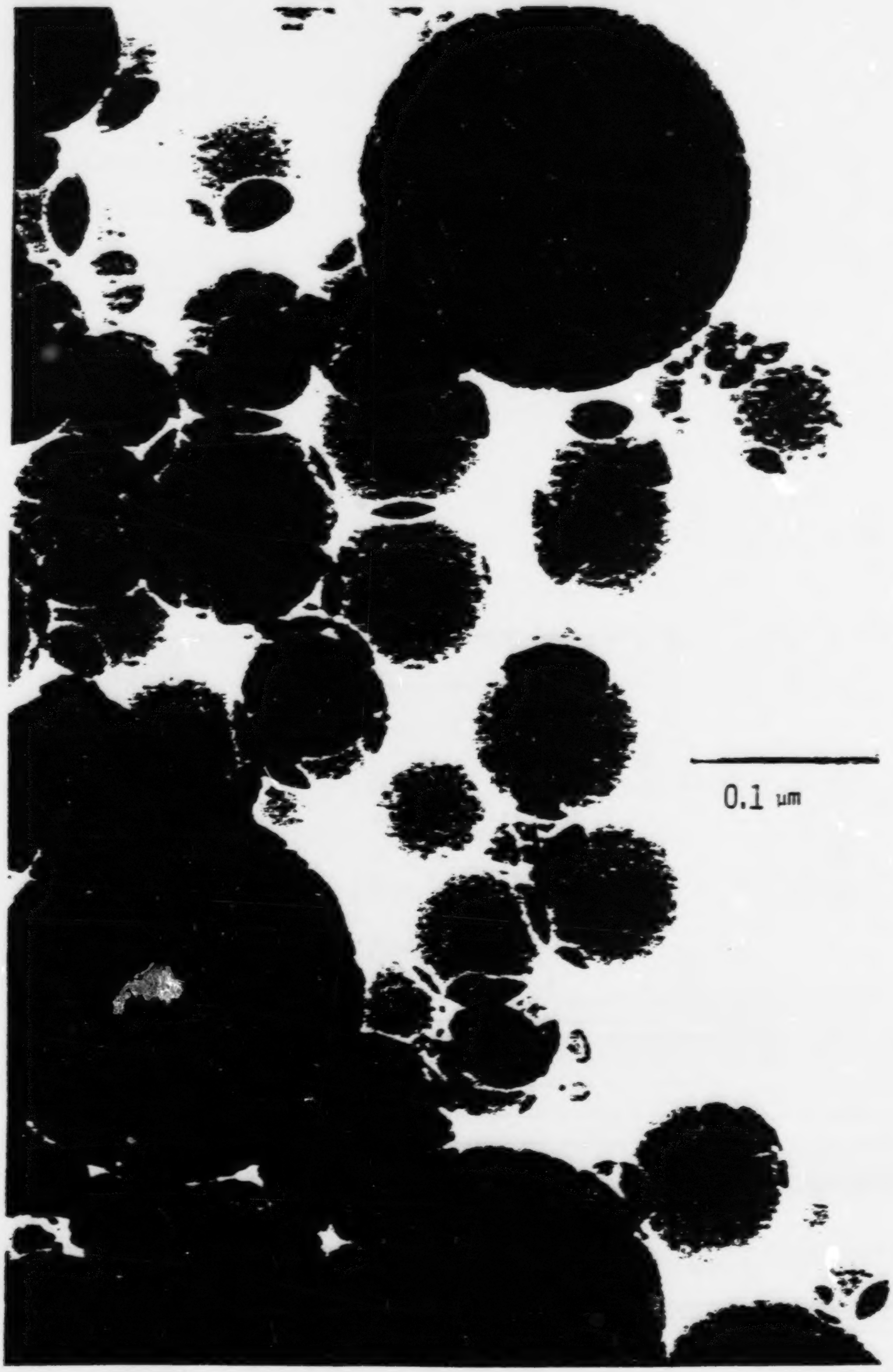

FIGURE 2. Condensed silica fume grains.

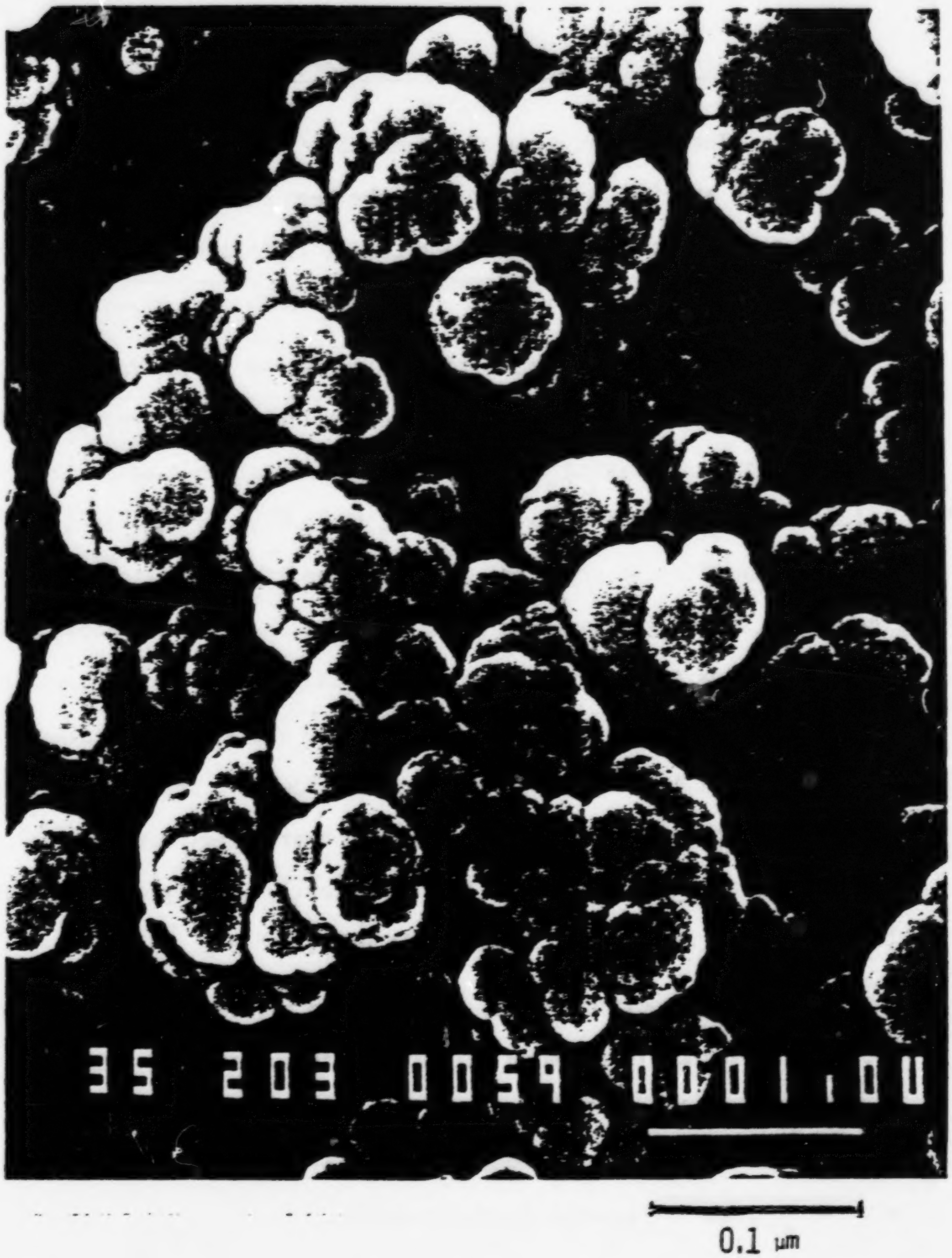
35 203 0059 0001.0U
0.1 μm

FIGURE 3. Condensed silica fume grains at very high magnification.

2.2 Physico-chemical characteristics of condensed silica fume

The specific area of condensed silica fume is exceptionally high, values as high as 20 000 m^2/kg have been reported (2); by comparison the surface area of portland cement is in the order of 300 to 500 m^2/kg.

The chemical composition of condensed silica fume depends on the composition of the silicon or ferrosilicon alloy produced. The most important difference in the chemical composition lies in the iron oxide content. This iron oxide content is as high as 5% when a 75% ferrosilicon alloy is produced, and less than 1% when silicon is produced. The sum of the silica and iron oxide contents is generally above 90%, the loss on ignition in the order of 3 to 5%, and the carbon content from 2 to 5%. The content in $A\ell_2O_3$, MgO, CaO and alkalis is always very low as can be seen in Tables 1 and 2. However, for a given plant, whatever the type of silicon or ferrosilicon produced, the chemical composition of the condensed silica fume usually is very constant due to the high purity of the raw materials used, Table 2.

The specific gravity of condensed silica fume varies from 2,0 to 2,20, which is a common value for vitreous silica. Its bulk density is very low, 0,2 to 0,3 t/m^3 (15 to 20 lb/cu. ft.)-a cement sack filled with silica fume would weight only about 10 kg compared with 40 kg when filled with portland cement-.

Silica fume normally is light grey to grey in colour, depending on the content of iron and carbon.

Components Types	SiO_2	Fe_2O_3
Silicon	> 92%	< 1%
Ferrosilicon 50%	> 90%	≈ 2 @ 3%
Ferrosilicon 75%	> 85%	≈ 4 @ 5%

TABLE 1. Comparison of the chemical composition of various condensed silica fumes.

	SILICON	FERROSILICON
SiO_2	93,7 ± 0,2	87,3 ± 1,0
Al_2O_3	0,3 ± 0,03	1,02 ± 0,1
Fe_2O_3	0,78 ± 0,05	4,44 ± 0,5
MgO	0,22 ± 0,01	0,34 ± 0,02
CaO	0,22 ± 0,01	0,44 ± 0,04
Na_2O	0,15 ± 0,07	0,20 ± 0,03
K_2O	0,48 ± 0,05	0,63 ± 0,03
C	2,6 ± 0,19	4,3 ± 0,06
S	0,15 ± 0,02	0,22 ± 0,03
L.O.I.	2,85 ± 0,07	4,6 ± 0,75
	5 samples	5 samples

TABLE 2. Variation in the chemical composition of condensed silica fume from silicon and ferrosilicon production

As can be seen from this description, condensed silica fume is really a unique and very attractive material because of its fineness and purity, however, as noted, handling can present problems.

2.3 Handling and transportation of condensed silica fume

Silicon and ferrosilicon producers have always had to face the problem of handling and transporting condensed silica fume to disposal sites or to customer's plant. Condensed silica fume is so fine that it is practically impossible to contain it in a dry form in any kind of container. They can be bagged in paper or plastic bags with difficulty but removal of the product from these bags without generating dust clouds continues to present problems.

Condensed silica fume has been granulated successfully (2,3), but again granulation without generating dust cloud is a problem. The only practical solution is for silicon or ferrosilicon producers to sell their condensed silica fume in a slurry form, when the customer can accommodate it. In this case each ton or condensed silica fume must be mixed to 1 ton of water. This high amount of water necessary to overcome the dusting problem is not necessarily an advantage in transportation and when considering possible further uses. Moreover, if a profitable market could be found for condensed silica fume, it should be capable of absorbing the condensed silica fume production on a year-round basis (Most electric arc furnaces are operating 24 hours a day, 365 days a year).

As the production from a single furnace is not very large in terms of mass, 5 000 to 10 000 t/y, it is not economical for the silicon or ferrosilicon producer to have 2 or 3 types of conditioning for its production. Furthermore, because the unit price of silica fume is quite low, he cannot invest too much money into storage facilities to enable him to sell this product according to the market demand.

A key factor in marketing condensed silica fume is the ability to process this finely divided material. Sherbrooke University has developed agglomeration processes that could be used to make the handling of condensed silica fume as easy as that of other powders such as portland cement and stone dust.

3. AGGLOMERATION OF CONDENSED SILICA FUME

With the patented processes developed at Sherbrooke University condensed silica fume can be either agglomerated in the form of a friable powder (3) with an apparent grain size distribution of a fine sand, Figure 4, or in the form of very hard and resistant granules that resemble fine crushed stone (4). Samples of these two types of agglomerated condensed silica fume are compared with an equal mass of non-agglomerated condensed silica fume and pelletized silica fume in Figure 5. After agglomeration the condensed silica fume occupies a volume 2,5 to 3,5 time smaller than in bulk.

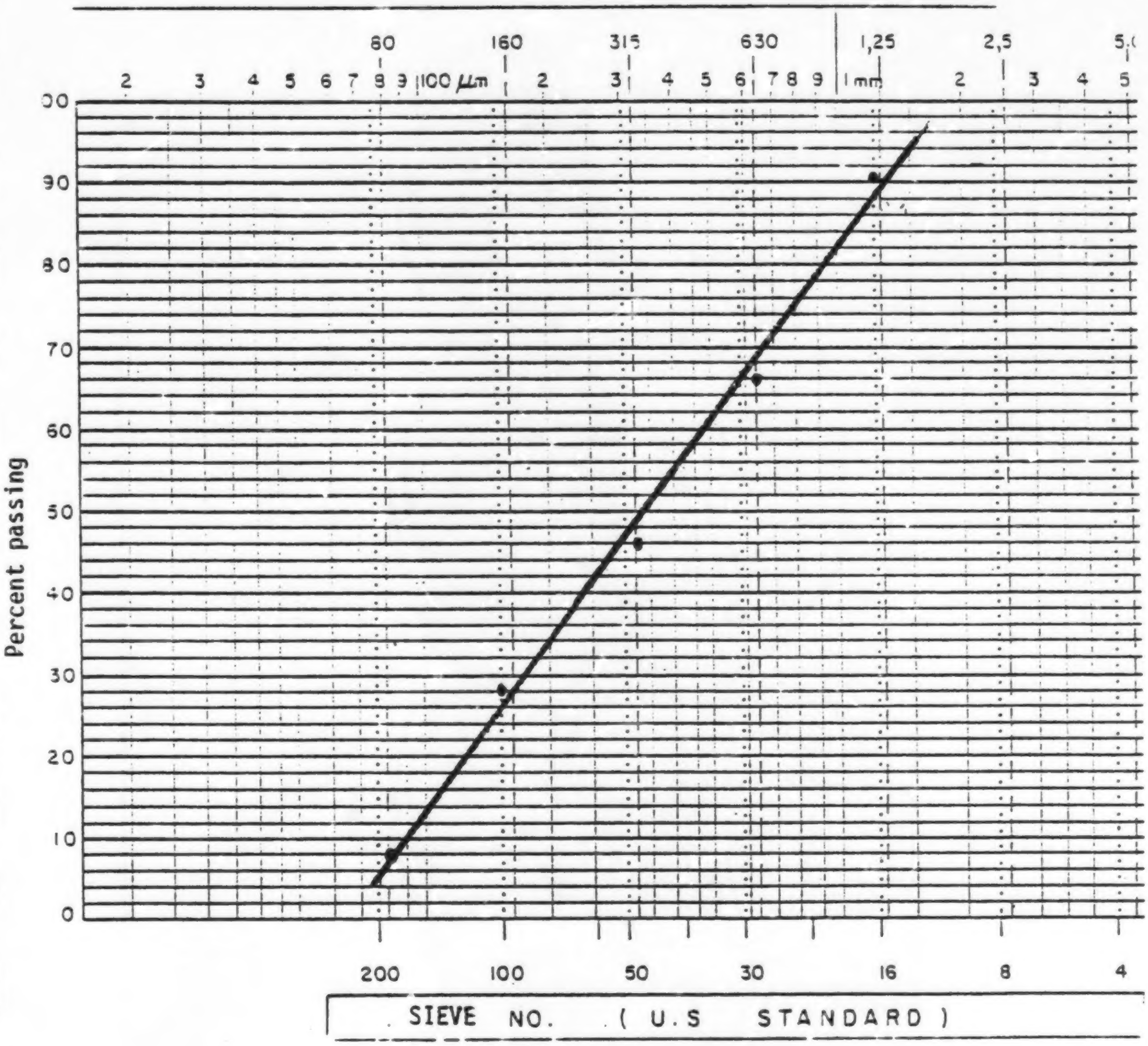

FIGURE 4. Agglomerated condensed silica fume.

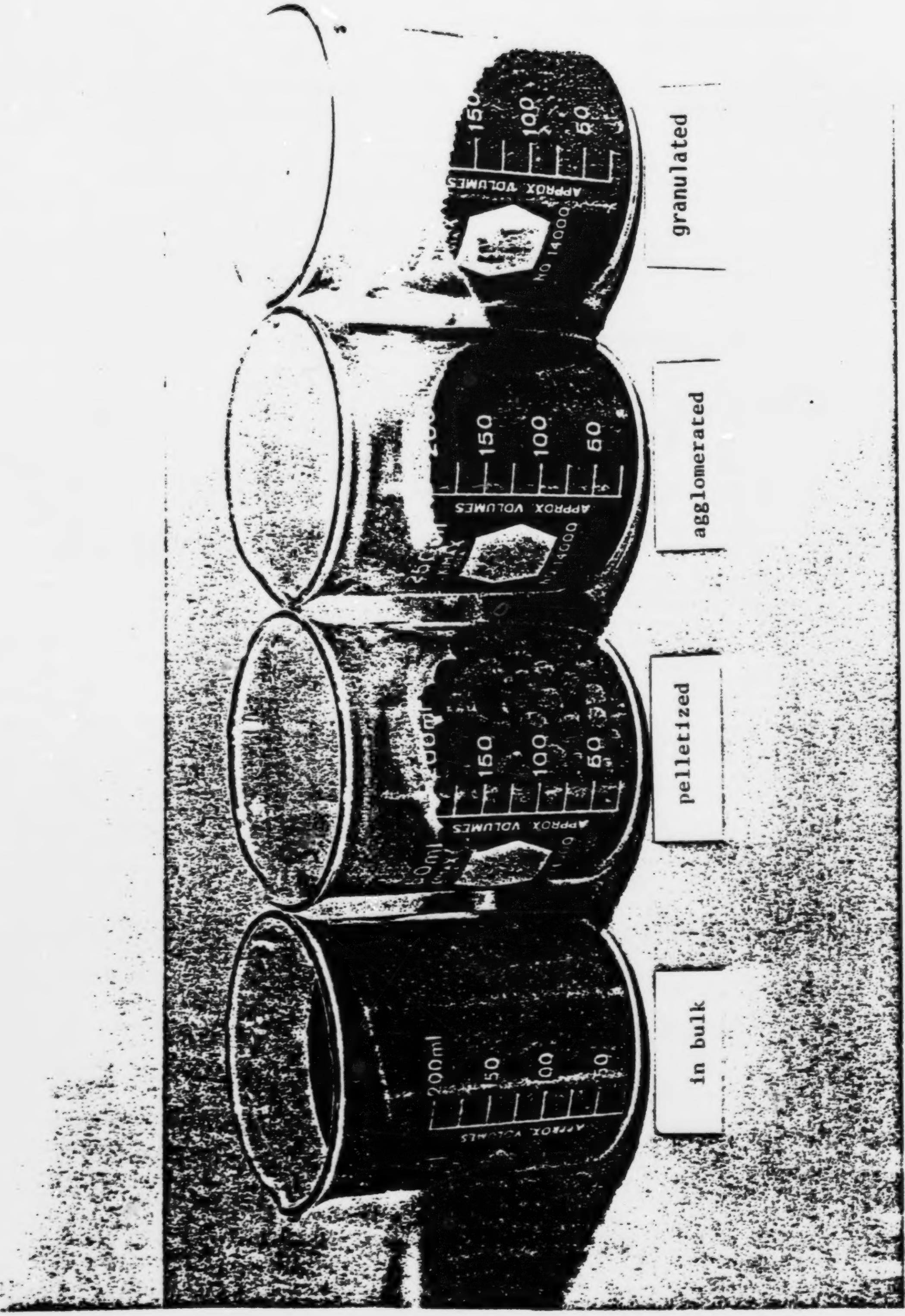
granulated
agglomerated
pelletized
in bulk

FIGURE 5. Aspect of agglomerated silica fumes.

3.1 The agglomerated friable powder

The principal advantage of agglomeration is that the powder can be handled, transported, stored, weighed in the same manner as cement or fly ash, using similar equipment without creating any particular dust problem. When introduced into a mixer, this powder can be easily disintegrated and dispersed in the mix as if it had been introduced in bulk. The friable agglomerated powder can easily be transported in bulk as a normal filler or shipped in paper or plastic bags.

3.2 The hard granules

If for some reason there is no immediate market for agglomerated condensed silica fume, they can be transformed into very hard and weather-resistant granules. These granules can easily be transported in an open truck box covered by a canvas and stored in a dump without creating any pollution or environmental contamination. Moreover these hard granules can be stored under water for a long time without showing any sign of disintegration.

4. POTENTIAL USES OF CONDENSED SILICA FUME

Condensed silica fume can be used by a great number of industries and, because they will be more accessible in the future, new markets will probably be developed. As reported by Erik Hallgren, (1) the most interesting markets seem to be: the addition of condensed

silica fume to concrete or to cement; the use of condensed silica fume as a binder and anti-caking agent in pellets or as a soil fertilizer; for the manufacture of refactory materials; and as filler in some types of rubber products and in thermoplastics.

5. AVAILABILITY

In Canada there are presently three sources of condensed silica fume, all situated in the Province of Quebec. Production is in the order of 20 000 to 30 000 t/y. Two US sources located in the Niagara Falls area would be of interest for the Toronto area. In the United States the total production varies from 300 000 to 500 000 t/y (5), and, in Norway, it is 140 000 t/y (6). These amounts are not expected to increase in a near future.

6. CONCLUSION

Condensed silica fume can be handled as easily as any other industrial powder if properly agglomerated, using the techniques outlined in this paper. Agglomeration should encourage the use of this unique material in a wide variety of applications.

However, the key factor that finally will determine the use of the condensed silica fume in a particular market is economics, because condensed silica fume remains a by-product produced in very limited quantities which cannot be transported great distances.

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POOR

QUALITY

ORIGINAL